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INORGANIC CHEMISTRY

INORGANIC CHEMISTRY

THEORETICAL AND PRACTICAL

WITH AN INTRODUCTION TO THE PRINCIPLES OF CHEMICAL ANALYSIS INORGANIC AND ORGANIC

AN ELEMENTARY TEXT-BOOK

BY

WILLIAM JAGO, F.C.S., F.I.C.

NEW EDITION

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PREFACE

THE revised Directory of the Department of Science and Art issued in 1895 contained a number of very radical alterations in the Elementary Syllabus of Inorganic Chemistry. It follows that corresponding changes have become necessary, both in the methods employed by teachers and also in the text-books used by their students. In order to meet such requirements, the present text-book has been completely re-written and considerably enlarged. The favourable consideration shown to this book in the past has led the author to the conclusion that its mode of treating the subject met the requirements of other teachers as well as his own, and therefore in the present edition the original plan has been adhered to as closely as possible.

As before, full and complete directions are given for the performance of each experiment. As stress is laid on the importance of students being able themselves to make clear sketches, the figures given are drawn in the simplest possible manner, a course which, it is hoped, will be of service to those using the text-book. In providing for experimental work in analysis, the reactions are first given of those metals and acids required for the elementary course,

and then a special series of tables dealing with them only. The reactions of the additional metals and acids are also given, together with analytic tables as before, so that the book still also covers the advanced syllabus in analysis. An important feature of last year's alterations consisted of the addition of a course of work in which students are required to observe the effects of heat, etc., on materials supplied, and to identify any gas which may be evolved. With the view of affording exercises in work of this kind, a section on "The Identification of Gases" is introduced on page 326; it is suggested that this course of work may profitably precede the study of analysis.

As a means of calling students' attention to the materials exhibited on the lecture-table, the author recommends an object-demonstration to be given at the close of each lecture, and has, at the end of each chapter of the work, given a short *résumé* of the most important materials and apparatus used.

A number of experiments in quantitative work have been introduced in the chapter dealing with the laws of chemical combination by weight and by volume; these, it is hoped, will be of assistance to the student in grasping the facts of what is meant by " chemical equivalents," and, at the same time, afford such exercises in quantitative work as the syllabus requires.

In 1888 some alterations were made in this book in order to provide for the requirements of students preparing for the matriculation examination of the London University; these have not, in the present edition, been interfered with, so that it is hoped such students will still find the work equally useful. At

the discretion of their teachers, Science and Art Department students may omit this additional matter.

The writer feels that he cannot better conclude his preface than by, as on a previous occasion, thanking both reviewers and teachers for the kindness with which they have received the book in the past, and for the suggestions as to increasing its usefulness with which they have favoured him. The author trusts that, in his efforts to provide for the requirements of a newer generation of students, he will be fortunate enough to meet with the same measure of success.

<div align="right">WILLIAM JAGO.</div>

35, QUEEN VICTORIA ST., LONDON, E.C.,
    January, 1896.

CONTENTS

TEXT-BOOK

OF

INORGANIC CHEMISTRY

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CHAPTER I.

INTRODUCTORY.

1. Matter.—Although the objects we see around us differ so much among themselves in form, appearance, and character, yet there is one property they all possess in common, and that is *weight.* All such objects are attracted by the earth, and the reason why we find a thing to be heavy is that this earth-attraction, known as *gravitation,* offers the resistance called *weight* to any efforts made to raise things from the earth's surface. This property of weight is characteristic of all substances we are able to handle and examine. It is convenient to have one name that shall include all such bodies, and accordingly in English we employ the term *matter.* **Matter, then, is anything which possesses weight—that is, is acted on by gravitation.**

2. Kinds of Matter.—Matter exists in three distinct forms, known respectively as solids, liquids, and gases.

Solids.—As examples of solids, such common substances as stone or wood may be mentioned: that these possess

B

weight is shown by the fact that they offer resistance to being lifted from the ground, which resistance may be measured in several ways. Although the meaning attached to the term "solid" is very familiar, yet it will be well to express the same in words. **A solid is a form of matter in which the particles cohere so rigidly that the substance maintains its shape independently of support from surrounding bodies, and offers resistance to any efforts to change such shape.**

Liquids.—Water and oil are well-known examples of liquids; that they possess weight is also a familiar fact, for any vessel weighs more when filled with a liquid than when the liquid has been poured away. The general properties of liquids are also well known, their leading distinction being the readiness with which the particles glide over each other. In consequence, as a result of gravitation, a liquid adapts itself to the shape of the retaining vessel, and runs over if the level of the mouth of the vessel be depressed below that of the surface of the liquid. But although the cohesion between the particles of a liquid is not sufficient to impart the rigidity which is characteristic of a solid, it is yet important to remember that there does exist some cohesion or attraction between the particles of a liquid. This is readily shown by the following experiment :—

Experiment 1.—Attach a clean glass plate *a*, about 4 or 5 inches in diameter, to pieces of wire *b, c, d*, in the same way as a scale pan is suspended from the end of the arm ; place it in a basin of water *e f*, so that the glass plate just floats on the surface. Notice the pull necessary to tear it away from the water and overcome the cohesion existing between its particles. To approximately measure the amount of this attraction or cohesion, suspend the glass plate and wire attachment from the hook *g* on one end of the arm of a balance, as shown in Fig. 1. Counterpoise in air by placing weights on the lighter side *h ;* then arrange a shallow basin, *e f*, filled with water (evaporating basin) underneath the glass plate, and raise the basin or lower the balance beam until the plate, as before, just floats on the

water. Add weights on the weight-pan *h* until the glass plate is thus separated, with a layer of water on its under side, from the main body of water in the basin.

Again expressing our meaning in a definition, we have : **a liquid is a form of matter in which there is some cohesion between the particles, but not sufficient to enable the substance to retain its shape against gravitation, independently of support from a rigid containing-vessel.**
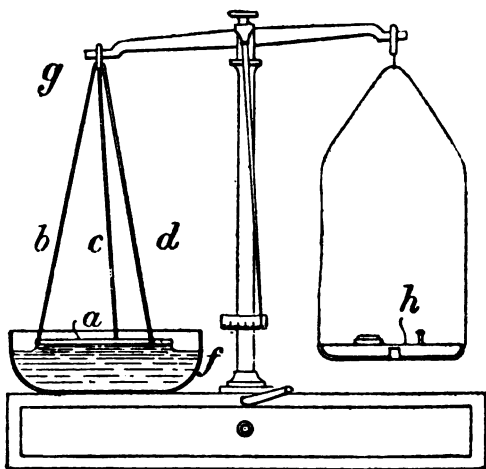
FIG. 1.—Cohesion of water.

Gases.—The existence and properties of gases are not so readily shown as are those of solids or liquids, still it is easy to demonstrate that gases are a form of matter, inasmuch as they possess weight. The earth is enveloped in a mixture of gases, which is known as "the air," or "the atmosphere," and on this gaseous mixture we may make our experiments.

Experiment 2.—Procure a stout round-bottomed flask about 5 inches diameter ; thoroughly clean and dry the interior, and fit to it an indiarubber cork through which passes a glass

tube in which is a stop-cock, as shown in Fig. 2, A, *o, n, m*. With
the stop-cock open, invert the flask and plunge it into a glass
jar of water (Fig. 2, A), and notice that the water does not enter
the flask. Take out the flask, wipe it absolutely dry, and weigh
as accurately as possible in a suitable balance. Make a note
of the weight. Next exhaust the flask as completely as possible
by means of an air-pump.

For laboratory purposes, a " Körting's " water-pump, arranged
as shown in Fig. 3, is well adapted. The pump itself is a small
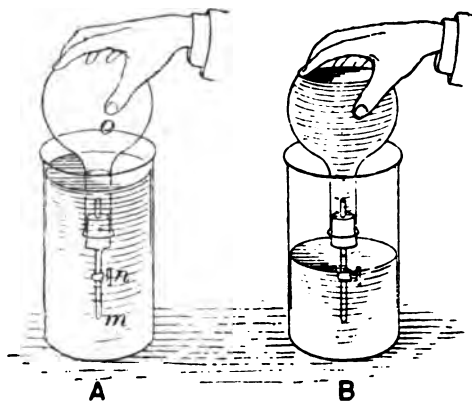
FIG. 2.—Air-filled, and empty flask, plunged into water.

brass instrument, *b ;* this must be securely fastened to an ordinary
high-pressure water supply tap, *a*. The connection may be
made by means of canvas-lined indiarubber hose-pipe, tightly
wired both to the pump and the nozzle of the tap. The side
inlet of the pump, *c*, is connected by means of a glass tube, *d e f,*
to a small bottle, *g*, the mouth of which is fitted with an india-
rubber cork. In this tube is fitted a glass stop-cock, *e*. In the
bottom of this bottle is a layer of mercury, *h*, about an inch in
depth. From as close to the bottom as possible of the flask *g*
leads an upright glass tube, *i j*, the length of which must be
at least 36 inches. A return tube, *k l*, is led down to a con-
venient height above the working bench, and to the open end
is attached any vessel or apparatus it is wished to exhaust.
The pump stands over a sink, and its lower end *p* must be

slightly below the mouth of an open wide-mouthed bottle, *q*. In use, when a stream of water is driven through the pump, the peculiar shape of the passage through, indicated by dotted lines in the figure, and shown to the right on an enlarged scale, induces a vacuum in the side tube *c*, and consequently any vessel attached thereto may be rapidly and almost completely exhausted of air. The small mercury bottle *g* and tubes *i j*, *k l*
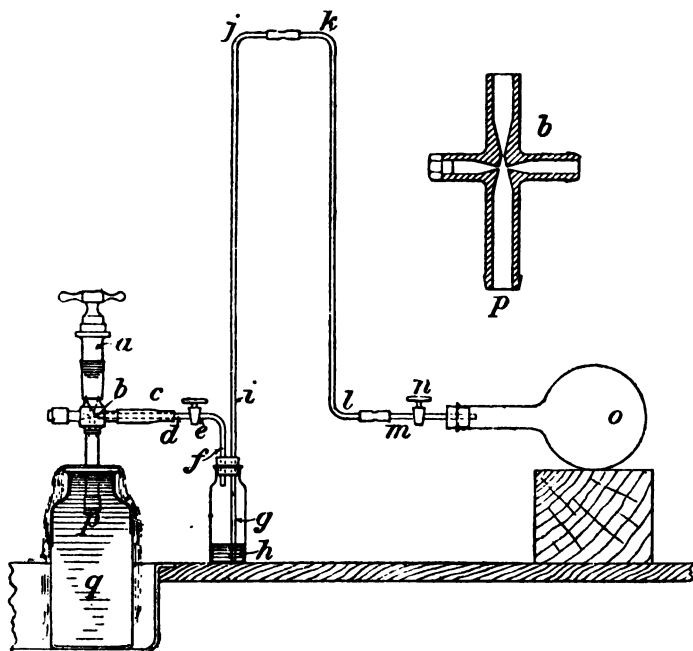
FIG. 3.—Water air-pump and flask arranged for exhaustion.

serve a double purpose. In the first place, they act as a water-trap, preventing any water from the pump finding its way by accident over into the vessel being exhausted ; and, secondly, they serve as a gauge by which the amount of vacuum can be measured, for, on shutting off the water, the mercury rises in *i j* to a height proportionate to the degree of exhaustion. With one of these pumps, a vacuum is readily obtained in which the

height of the mercury in *i j* stands within an inch of that in the mercurial barometer.

In our experiment, connect the weighted flask and tube *m n o* with the end *l* of the air-pump tube ; shut both the stop-cocks *e* and *n*, and turn on the water through the tap *a ;* notice that as it escapes from *p* and overflows the bottle *q*, no air-bubbles are perceptible. Open the stop-cock *e*, and speedily the air is exhausted from *g*, a stream of bubbles being observed to escape through *p*. When the bubbles cease to escape, open the tap attached to the flask *n*, and observe again the escape of a stream of air-bubbles through the pump. Allow this to pro-ceed until no more air is seen escaping; then slowly turn off the water, and notice the mercury rise in the tube *i j*. This rise should amount to about 29 inches. Turn off the stop-cock *n* fixed to the flask, and detach it carefully from the pump tube at *l*. Again weigh the flask as carefully as possible, and note the weight, which will be less than that before the air was exhausted. The difference between the two weights is that of the air which has been removed. Next invert the flask, and place the end of the tube *m* below water as in Fig. 2, B ; open the stop-cock very gently, and the water rushes in and nearly fills the flask. Take out the flask, disconnect the cock and tube *m n*, pour the water into a measuring-vessel, and thus determine the quantity. This gives the volume of air which was removed by the pump, the weight of which volume is already known. From these data, calculate the weight of one litre of air.

We learn from this experiment, first, that air occupies space, and that when the flask is, as to start with, full of air, water cannot enter. We next learn that air possesses weight, and consequently is a form of matter. We see also that water rushes into the flask when absolutely empty, *i.e.* deprived of air. Our experiment tells us roughly what the actual weight of air is; its performance in the author's laboratory gave the following results :—

Weight of flask before exhaustion . . 237·48 grams.

„   „   after   „   . . 235·80 „

Weight of air which had been exhausted . 1·68 „

Volume of air which had been exhausted
    from flask, as determined by admitting
    water and measuring quantity .   .   1430 c.c.
    The weight of one litre (1000 c.c.) is therefore—

$$\frac{1000 \times 1\cdot68}{1430} = 1\cdot175 \text{ grams.}$$

The accepted weight of air as determined by more
exact methods under the conditions of the experiment is
approximately 1·207 grams per litre.

As in the case of liquids, the particles of gases move
readily over each other, as is shown by the fact that the
air contained by the flask was exhausted through the small
tube passing through the cork. Both liquids and gases
possess the property of flowing, and are classed together
as *fluids*. One very important particular in which gases
differ from liquids is that the particles of a gas always tend
to fill the space in which they are confined ; while a liquid
remains at the bottom of the vessel, as, for example, in a
glass partly filled with water. Air, being colourless, is
invisible, and one cannot tell by looking whether a flask is
full or empty. But if the experiment just described be
made on a flask filled with chlorine, which is a gas of a
yellow colour (or preferably on some other even more darkly
coloured gas), it will be seen, as the gas is exhausted, that
the flask does not become partly empty. On the contrary,
the flask remains full, but the colour of the gas gradually
becomes paler and paler, until finally, as the last traces of
gas are exhausted, there is only the faintest possible tinge
of colour permeating the whole flask. From this we gather
that the particles of gas are self-repellent, cohesion being
entirely destroyed, and the gas tending to occupy as great a
space as possible. A gas, therefore, is a form of matter
in which no cohesion exists between the particles, which
instead are self-repellent, and cause the gas to expand

itself so as to occupy the whole of the space in which confined.

In many instances, one and the same kind of matter can exist in the three different states of solid, liquid, and gas ; as, for example, water, which assumes the three forms of ice (solid), water (liquid), and steam (gas).

3. Force.—It would, at first sight, seem that the definition of matter already given is sufficiently extensive to embrace everything, but yet a moment's consideration will show that there are other things beside matter. To give an illustration : you know that a hammer-head consists of matter because it possesses weight, but if with this hammer you give a series of blows to a small piece of nail rod, you have given something which is not matter. The hammer-head is not lighter, neither is the piece of nail rod heavier. Still the blows are something, as otherwise they could produce no effect. For one thing the piece of nail rod will have been flattened and altered in shape ; further, and of more importance to us at this moment, it will have become hot to the touch. Again, to mention another example, if a dry brick be most carefully weighed, and then made red-hot in a furnace, the hot brick weighs precisely the same as it did when cold. Further, if it be allowed to cool, this hot brick imparts heat to surrounding objects, and nevertheless remains unaltered in weight. Here, then, we have something very definite, which a body can receive and again yield, and which is not matter. Let us try to see what relationship this something has to matter ; in the first illustration, the blows were struck by the moving hammer-head, which consists of matter in motion. The more rapid the motion, the more violent would be the blows ; in fact, the force of the blow depends both on the quantity of matter and the rapidity of its motion. Further, although outside any attempt at present proof, the hot iron of the nail rod, and also the hot brick, differ from the same substances in the cold state, in that their component particles are in a

state of movement; as these substances cool, the particles once more enter into a condition of comparative rest. This something, then, beyond matter is closely associated with motion, and is termed *force*. **Force is defined as that which is capable of setting matter in motion, or of altering the direction or velocity of matter already in motion.** The motion of bodies may be divided into two classes: there is first that of the body as a whole, as in the case of the moving hammer-head; secondly, the internal movement of the particles of a body, as when it becomes hot.

4. Object of Chemistry.—It is now easy to explain the objects of chemistry. Matter is not only most varied in form, but its form is also continually varying; it is the function of the chemist to investigate these changes, and also the nature of the substances which participate in them. In short, **chemistry is that science which treats of the composition of matter, of the changes produced therein by heat and other natural forces, and of the action and reaction of different kinds of matter on each other.**

5. Chemical as distinguished from Physical Changes.—It is necessary to learn to distinguish between what are simply alterations in the physical properties of matter, and what are really chemical changes. To investigate this the following experiments may be made:—

Experiment 3.—Heat a piece of platinum wire in the flame of a Bunsen gas lamp; it immediately becomes white hot: remove it, and, as the wire cools, it once more regains its original brightness. It is not in the least altered, not even tarnished.

Next heat in the same way a piece of *bright* iron wire: this is tarnished, but otherwise will have undergone no great change.

Next place a piece of magnesium wire or ribbon in the flame: it burns with a dazzling white light, depositing a white, easily powdered body, composed of oxygen and magnesium, and known as magnesia.

In the first case the change produced is merely physical,

and although the hot wire possesses properties which are absent in the cold, yet on the wire losing its heat it again regains its previous characters. With the iron wire a slight permanent change is produced on the surface : this is of a chemical character, but the main portion of the wire is unaltered. In the third instance a vigorous chemical change has occurred; the magnesium, as such, has entirely disappeared, and a new body takes its place. The student hereby learns that **chemical changes are distinguished from those of a merely physical character by more or less striking permanent alterations in the appearance and properties of the substances involved therein.** The following are additional examples of changes produced by chemical action.

Matter frequently, as a result of chemical action, changes its conditions; thus liquids may be converted into solids, solids into gases, and gases into solids.

Experiment 4.—Place in a test-tube some dilute sulphuric acid, in another about the same quantity of solution of calcium chloride; notice that each is a transparent, colourless liquid. Add the one to the other; in a few seconds the whole has become a solid mass, and the test-tube may be inverted with only a few drops of liquid running out. In this case a new body has been produced, called calcium sulphate, which combines with a large portion of the water present to form a solid.

FIG. 4.—Jars of ammonia and hydrochloric acid.

Experiment 5.—Having previously filled two dry jars respectively with hydrochloric acid gas and ammonia gas, invert that containing the hydrochloric acid over the jar containing the ammonia (Fig. 4), and withdraw both the covering plates. Dense white fumes are immediately formed, and settle as a white powdery mass on the inside of the jars. Notice at the same time that the jars become distinctly warm. The solid substance formed in this experiment is that known as ammonium chloride.

One of the most striking illustrations of the conversion of a solid into gases is the burning of an ordinary candle. To all appearances the candle itself vanishes and is completely lost; nevertheless, it is very easy to trace its components after the candle has disappeared.

Experiment 6.—Light a piece of candle—the solid fat, composed of hydrogen and carbon, changes into gaseous compounds. Hold a cold surface, as the outside of a porcelain dish filled with water, in the flame: it gets blackened, owing to the separation of carbon as soot or lamp-black; it also becomes wet, through the deposition of water produced by the combination of hydrogen with the oxygen of the atmosphere.

Pour into a glass gas jar, or colourless glass bottle, of about a pint capacity, a layer of half an inch of clear lime-water; shake up the jar—the lime-water remains clear. Next take a small piece of candle and fix it in a deflagrating spoon; light it and place in the glass jar; it soon goes out. Again shake the jar—the lime-water now becomes turbid through the formation of a compound of lime and the carbon dioxide produced by the oxidation of the carbon of the candle.

The small wax tapers used for lighting Christmas trees, etc., are very suitable for these experiments.

Although, in burning, the candle is lost as such, the bodies of which it is composed can thus be traced; for the disappearance of the candle is accompanied by the production of water, and also an invisible gas, which evidently differs from ordinary air, because it turns the lime-water milky, while, as the student will have seen, air is unable to produce this change.

6. Indestructibility of Matter.—Although chemical action can produce such marvellous changes, yet there is one thing it cannot do—it can neither create nor destroy matter. An illustration of this latter point is afforded by the burning candle described in the last paragraph; but the same experiment, when performed under more exact conditions, shows not merely that the products of the

burning candle can be traced, but also that they more than fully equal in weight the original candle itself.

Experiment 7.—Take a glass chimney, *a* (Fig. 5), such as is used for Argand lamps ; fit a cork to each end ; bore several holes in the lower cork, one being in the centre and of a size to fit a small taper, which must be inserted in it, *b*.   Bore a single hole through the upper cork, through which pass a piece of glass tubing bent at right angles.   Procure a U tube *c d;* fit it with corks and bent-glass tubes, as shown in Fig. 5 ; fill this tube with small fragments of sodium hydrate (caustic soda). Obtain a two-gallon can with stop-cock at bottom, and fitted with cork and glass tube, *f g*, through the mouth ; fill this can with water.   Suspend the chimney *a* and U tube *c d* by means
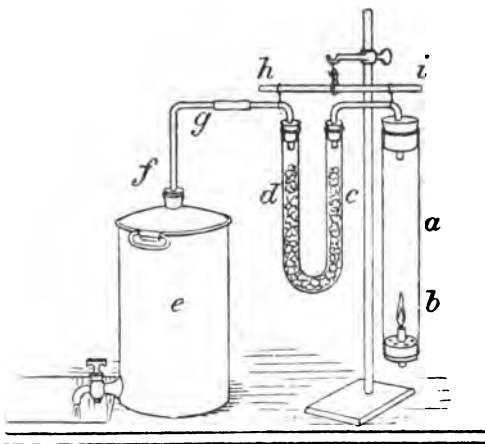
FIG. 5.—Apparatus for weighing products of combustion of candle.

of thin wire to a small wooden rod, *h i ;* weigh these together as carefully as possible, and note the weight.   Then connect up the whole apparatus as shown in the figure, suspending *a*, *c d* from a retort or other convenient stand.   Open the stop-cock of the can, and as the water runs out it causes a current of air through the apparatus.   Take out the taper, light, and quickly replace it ; allow it to burn for three or four minutes.   Then turn off the cock—the taper goes out ; disconnect the chimney and

U tube and again weigh. The weight has increased, owing to oxygen having been taken up from the atmosphere by the burning taper; it has combined with its constituents to form water and carbon dioxide respectively. These compounds are both absorbed and retained by the sodium hydrate.

In this way proof is obtained of the fact that the products of combustion weigh more than the original substance burned, the increase being due to the oxygen with which the substance has combined. This experiment, although striking, is incomplete, because no account has been taken of the weight of the oxygen before its combination with the candle. Our knowledge thus obtained is supplemented by the following experiment :—

Experiment 8.—For this experiment a special piece of apparatus, shown in Fig. 6, is required. This consists of a glass flask of some 250 cubic inches (4 litres) capacity, fitted with a stop-cock, and two wires, *a, b,* passing through the cork and connected at the lower ends by a piece of fine platinum wire. Around this wire wrap lightly a piece of gun-cotton, weighing about from 0˙8 to 1˙0 gram, and introduce into the flask. Connect up the stop-cock of the flask to the Körting's air-pump previously described, exhaust as completely as possible, shut off the stop-cock, disconnect the flask, and weigh. Next connect the wires *a, b* to an electric battery, giving sufficient current to make the platinum wire red hot. This ignites the gun-cotton, which completely disappears with a bright flash. Again weigh the flask—it will be found to remain unaltered in weight.

FIG. 6.—Apparatus for weighing products of combustion of gun-cotton.

As a result of being heated, the gun-cotton has undergone a chemical change by which it has been converted into gases; these, however, weigh precisely the same as

did the original gun-cotton. The result of this and all other similar experiments is summarized in the statement that **matter is indestructible, and consequently the same weight of material remains after any and every chemical change as there was before its commencement.**

7. Mechanical Mixture and Chemical Combination.—It is important to learn to distinguish between these two different processes, and this end is best attained by the study of a typical experiment.

Experiment 9.—Take some finely divided copper; notice its colour; mix intimately with powdered sulphur; the mixture has a tint intermediate to that of the substances when separate. Place some of the mixed powder in an evaporating-basin, and wash with a gentle stream of water; notice that the sulphur is carried away, and that the heavier copper remains behind. This and several other methods may be employed to effect their mechanical separation, which is easily done, as there is no union between them. Next place some of the mixture in a dry test-tube, and heat; observe that the sulphur first melts, and that shortly after the whole mass glows brightly. When cool, examine the resulting substance; it is of a bluish-black colour, brittle, and one of its ingredients can no longer be separated from the other by the action of water or mere solvents. A new body has been formed by the union of the sulphur and copper, known as copper sulphide.

This and also several of the preceding experiments show that **chemical combination is widely different from mere mixture.** In the latter case the resultant body is a mean in appearance, specific gravity, etc., between its constituents: they still each possess their individual properties, and the separate particles may be seen with sufficient magnifying power. In the former the body produced is more or less different in appearance and properties from those of which it is composed. Further, as will be completely demonstrated at a later stage, when the substances chemically combine they invariably do so in definite

proportions. In a mixture, the substances may evidently be present in any proportion whatever.

8. Heat produced by Chemical Combination.— Not only does chemical combination produce bodies different from a mixture of the constituents, but it is also accompanied by an evolution of heat. In addition to the proofs of this statement afforded by previous experiments, the following shows the production of heat by chemical combination in a striking manner.

Experiment 10.—Place a few fragments of recently burned quicklime in a saucer or evaporating-basin, and pour in sufficient cold water to just moisten the lime. In a short time the lime becomes very hot, and the water as such entirely disappears.

The heat in this experiment is due to chemical combination between the water and the quicklime.

The difference in appearance of bodies as a result of chemical combination and the production of heat are two of the principal characteristics by which a chemical union between substances is detected.

9. Synthesis and Analysis.—In the last two experiments performed the operations have been of the kind known as "synthesis," that is, the putting together of substances and building up new bodies. Another most important mode of chemical investigation is "analysis," which consists of decomposing bodies, revolving them into substances of simpler composition.

Experiment 11 —Place some red mercuric oxide, about as much as could be held on a threepenny piece, in a dry test-tube ; close the mouth *loosely* with the thumb and apply heat. Notice that the colour changes from red to black, the oxide gradually disappears, and minute globules of metallic mercury condense on the upper part of the tube. Next light a splinter of wood (a match will do very well) ; when well lighted blow out the flame, and introduce it while still glowing into the tube ; it immediately again bursts into flame, thus showing the presence of the gas called oxygen.

In this experiment a compound has been separated into its two simpler bodies; or, in other words, its analysis has been effected.

10. Element, Compound, Mixture.—Experiments already made have shown that certain substances can be split up into different substances; but there are a certain number of bodies which cannot by any known means be thus decomposed. These latter are termed elements, while bodies produced by the combination of elements are called compounds.

An **ELEMENT** is a substance which has never been separated into two or more dissimilar substances.

A **COMPOUND** is a body produced by the union of two or more elements in definite proportions, and consequently is a substance which can be separated into two or more dissimilar bodies. Compounds differ in appearance and characteristics from their constituent elements.

The term **MIXTURE** is applied to a substance produced by the mere blending of two or more bodies, elements, or compounds, in any proportion without union. Each component of a mixture still retains its own properties, and separation may be effected by mechanical means.

11. Relation of Chemical Action to Force.— It has been already stated that when chemical combination occurs heat is generated; in order to effect the change described in the last experiment heat has been used and has disappeared as such, being stored up in the elements in the form of the available or potential energy of chemical attraction or affinity. If the mercury and oxygen are again caused to combine, the act of reunion will once more set free the exact amount of heat that was necessary to effect their decomposition. Many instances are known in which bodies that evolve a certain amount of heat on uniting may be again decomposed by being subjected to a more intense heat. In all such cases **the quantity of heat evolved**

during chemical combination is exactly equal to that requisite to effect the decomposition of the resultant body.

Further, by proper appliances the chemical action of elements entering into combination may be caused to produce electricity; and electricity in its turn is competent to dissociate the elements of compound bodies. There is in this case also a definite relation between the amount of chemical action and the quantity of electricity produced.

Force having been defined as that which is capable of setting matter in motion, it follows that chemical combination must be ranked among the forces; for such chemical actions, of which the combustion of coal is a typical example, generate heat, and thus indirectly, as in the steam-engine, constitute our most valuable means of setting matter in motion and overcoming resistances generally.

12. Relation between Gravitation, Cohesion, and Chemical Attraction.—Matter is maintained in its normal state through the Universe by the action of three most important forces—gravitation, cohesion, and chemical attraction. The first of these acts through all space, and exerts an attraction between all matter. Cohesion acts only across non-appreciable distances, holding together the particles of solids, and also, though to a much less extent, those of liquids.

By means of heat this force may be often overcome; thus solid ice may be converted into water; a further increase of temperature destroys the remaining cohesion and produces steam, which, in common with all other gases, is devoid of any cohesion between the particles. But, whether as ice, water, or steam, the substance is the same in chemical properties. By application of a more intense heat, however, the steam is decomposed into oxygen and hydrogen. Heat, therefore, not only destroys cohesion, but, when sufficiently intense, overcomes the force of chemical attraction which holds the elementary atoms of all compound substances together.

C

Summary.

Nature of matter—Different kinds of matter, solids, liquids, and gases, and their properties.

Force, and its nature.

Objects and definitions of chemistry. Physical and chemical changes.

Matter is indestructible ; in no chemical change is it lost.

Chemical combination is essentially different from mere mixture ; not only accompanied by change of appearance, but also by evolution of heat.

" Element," etc., defined.

Two most important types of chemical action, synthesis and analysis.

Heat is capable of effecting the decomposition or analysis of compounds. The quantity necessary is reproduced when the elements recombine.

Chemical action is a force.

Chemical attraction holds together the elementary particles of compound bodies. Heat overcomes it and dissociates them.

OBJECT DEMONSTRATION.

Note carefully the appearance and properties of the different substances used in the various experiments described.

Platinum is a white untarnishable metal ; iron is grey in colour, but tarnishes somewhat readily ; magnesium is white, with a superficial tarnish, but still distinctly metallic in character. Platinum is very heavy, while magnesium is light. Note the difference in character of magnesia, which is a white powder.

Observe that dilute sulphuric acid and calcium chloride solution are colourless liquids ; note the appearance of the white solid crystalline calcium sulphate.

Observe the appearance of the sodium hydrate fragments in Experiment 7.

Examine gun-cotton used in the following experiment ; note that it is similar in appearance to ordinary cotton or cotton-wool.

Examine copper as wire; note that it is very tough and soft ; also that when powdered it is of a reddish tint. Note that sticks of sulphur are very brittle. Look at the mixed powder, and observe its colour, and the separate particles of copper and

sulphur. Observe the bluish-black copper sulphide ; compare it with specimens of mineral copper sulphide.

Note the appearance of mercury oxide ; observe that it is heavy. Note also the liquid metallic character of mercury, and also that it is of very high density.

LABORATORY DIRECTIONS.

Several of the experiments described in this first chapter, although illustrating very simple facts, such as the weight of air, require skill and experience in chemical manipulation for their successful performance. The student will probably first be content with seeing them performed, and grasping the lesson they are intended to convey. Whether he will subsequently himself repeat the experiments must depend on the discretion of his teacher, who will, throughout the course of laboratory work, select for him such experiments as it is desirable he should himself make personally.

In the laboratory the student will either have to provide for himself, or be supplied with, a set of apparatus sufficient for the performance of the common experiments. Such a set should include—

Bunsen's burner and iron rose, with 2 feet of india-rubber tubing.

Retort-stand and spring clamp.

Two pieces of iron wire gauze 5 inches square.

Three flasks, respectively of 4, 8, and 16 oz. capacity.

Six test-tubes, 6 inches by $\frac{3}{4}$ inch diameter.

Test-tube brush.

Thistle funnel 18 inches long.

Glass funnel 2 inches diameter.

Dozen assorted corks.

Brass crucible tongs.

Small evaporating-basin, about $2\frac{1}{2}$ inches diameter.

Small beaker, $4\frac{1}{2}$ oz. capacity.

Two books of litmus paper, red and blue.

$\frac{1}{4}$ lb. small glass tubing.

Two feet small india-rubber tubing.

Four glass bottles.

Four ground glass plates.

The following apparatus is generally supplied for common use :—

Earthenware pneumatic troughs and beehive shelves.

Deflagrating spoons and caps.

Deflagrating jars, open at top and bottom.

Retorts of various sizes.

Cork-borers.

Pestles and mortars.

Aspirator, balance, weights, etc.

The more expensive pieces of apparatus must be obtained, when required, by application to the teacher.

The student should, in the first place, make himself familiar with the names and uses of his apparatus. Let him next carefully and thoroughly clean the glass and porcelain vessels. The chemicals required will be found as a rule in bottles and jars, so placed as to be readily accessible to the whole of the students. They should under no circumstances be removed from their places ; the quantity required should be taken in a flask or test-tube, and the bottle immediately restored to its place. A strict adherence to this rule prevents the loss of a great amount of time which would otherwise be spent in searching over the laboratory for bottles, etc.

In getting the chemicals for an experiment, be sure the right ones are taken ; see that concentrated acids are not used where dilute should be employed ; never use pure substances when the commercial will answer the purpose ; do not let the stoppers of bottles lie about or get mixed. Take no more of the substance than you require, and if you happen to have an excess do not return it to the bottle without express permission ; much confusion has been caused by chemicals being replaced in the wrong bottles.

When directions are given that substances are to be *mixed*, solid bodies are to be first *powdered*, and then stirred together until the mixture is as uniform as possible.

Heat is to be applied to tubes, etc., by means of the Bunsen burner ; before lighting it, see that the holes at the bottom are open ; the flame should be non-luminous ; if smoky, it is a sign that the gas is burning at the lower end of the tube of the burner ; it must be turned out and re-lighted. This catching fire at the bottom is the result of an excess of air entering; the remedy is to turn on more gas, or partly close the air-holes by

turning the ring of the burner over them. In heating test-tubes, the heat must be applied gently at first, with a constant motion of the tube, or, if the tube be fixed, of the burner.

If heating a liquid, never let the flame play on the part of the tube above its surface. When a solid is being heated, if any moisture happen to be present, it condenses in the upper and cooler parts of the tube ; when there is the slightest sign of this, hold the tube almost horizontal, but with the hot part rather the higher : this prevents the condensed water running back on the hot glass.

A laboratory note-book should always be kept, and an account entered in ink of every operation as performed. This applies with special force to weighing

At the close of the laboratory lesson wash the glass apparatus, and wipe with a dry cloth any water, etc., from the retort stand, and other articles which might rust.

Metric System of Weights and Measures.—For the complicated system of weights and measures in use in England, most chemists substitute the very simple metric system. The unit of the system is the metre, a rod of platinum deposited in the archives of France, which, when constructed, was supposed to be one-tenth-millionth part of the quadrant of a great circle encompassing the earth on the meridian of Paris.

Measures of Length.—The metre measures 39·37 inches. It is multiplied and subdivided by 10 for the higher and lower measures of length.

Kilometre	= 1000 metres	=	39370	inches.
Hectometre	= 100	.,	= 3937·0	,,
Decametre	= 10	,,	= 393·70	,,
Metre			= 39·370	,,
Decimetre	= 0·1	metre	= 3·9370	,,
Centimetre	= 0·01	,,	= 0·39370	inch.
Millimetre	= 0·001	,,	= 0·03937	,,

The Greek prefixes deca, hecto, and kilo are used to represent 10, 100, and 1000 respectively ; and the Latin deci, centi, and milli signify a tenth, hundredth, and thousandth.

The prefixes are used with the same meaning in the other measures. The decimetre is very nearly 4 inches in length : this affords an easy method of roughly translating measures of the one denomination into those of the other. The actual size of a decimetre is given in Fig. 7.

Measures of Capacity.—The measure of capacity is derived from that of length by taking one cubic decimetre as the unit : this is named the litre, the capacity of which and that of its derivatives in English measures are appended :—

				Cubic inches.	Pint.
Kilolitre	= 1000 litres	=		61027	1760·7
Hectolitre	= 100	„	=	6102·7	176·07
Decalitre	= 10	„	=	610·27	17·607
Litre			=	61·027	1·7607
Decilitre	= 0·1 litre		=	6·1027	0·17607
Centilitre	= 0·01	„	=	0·61027	0·017607
Millilitre	= 0·001	„	=	0·06102	0·0017607

Each side of this square measures

1 Decimetre, or

10 Centimetres, or

100 Millimetres, or

3·937 English inches.

A *litre* is a cubic measure of 1 decimetre in the side, or a cube each side of which has the dimensions of this figure.

When full of water at 4° C. a litre weighs exactly 1 *kilogram* or 1000 grams, and is equivalent to 1000 cubic centimetres ; or to 61·024 cubic inches, English.

A *gram* is the weight of a centimetre cube of distilled water; at 4° C. it weighs 15·432 grains.

1 sq. Centim.

4 inches.

Fig. 7.—Diagram showing size of 1 decimetre.

The litre being the capacity of a cubic decimetre, it is evident that the millilitre equals in volume a *cubic centimetre;* this latter term, or its abbreviation (c.c.), is very frequently used in preference to millilitre ; thus a pipette is said to contain 50 c.c., and a litre flask is often called a 1000 c.c. flask

A cubic inch is equal to 16·38 cubic centimetres.

Measures of Weight.—The weight of one cubic centimetre of distilled water at its maximum density (4° C.) is taken as the unit of weight, and is called a gramme or gram.   The subdivisions and multiples are again the same :—

				Grains.	Avoirdupois ounces.
Kilogram	=	1000 grams	=	15432·3	35·2739
Hectogram	=	100	„ =	1543·23	3·52739
Decagram	=	10	„ =	154·323	0·352739
Gram				15·4323	0·0352739
Decigram	=	0·1	gram =	1·5432	0·003527
Centigram	=	0·01	„ =	0·15432	0·0003527
Milligram	=	0·001	„ =	0·015432	0·00003527

A kilogram is a little over 2 lbs. 3¼ oz., and a hectogram 3½ oz.   An ounce avoirdupois equals 28·35 grams.

The relation between the weight and volume of water is seen to be a very simple one ; the volume being the same number of c.c. as the weight is grams.   With other liquids the volume in c.c. × specific gravity = weight in grams.

Experiment 12.—Take either a half-litre or litre flask ; see that it is dry, and weigh carefully ; fill to the graduated mark with distilled water, and again weigh ; the weight of the water is either 500 or 1000 grams.

English Weights and Measures. — Familiarity with English weights and measures is assumed ; still the following particulars may be useful :—

One gallon of pure water at a temperature of 62° Fahr. (16·6° C.) weighs 10 pounds, or 160 ounces, or 70,000 grains. The pint therefore weighs 20 ounces.   The measure termed a "fluid ounce" is derived from the weight of a pint of water. A fluid ounce is a measure of volume, not of weight, and equals one-twentieth part of a pint.   The fluid ounce bears the same relation to the avoirdupois ounce as does the cubic centimetre

to the gram. When directions are given to dissolve one part by weight of a solid in 5 or other number of parts by weight of water, either ounces in fluid ounces or grams in cubic centimetres may be taken. A gallon is equal to 277·274 cubic inches. An ounce avoirdupois weighs 437·5 grains.

The Balance.—In a laboratory there will be several balances of various degrees of delicacy, those used for purposes of analysis weighing to within one-tenth of a milligram. For ordinary elementary experiments such great sensitiveness is unnecessary, and a very useful form of balance is that shown in Fig. 8, a description of which is given. The use of this must be restricted to weighings in which accuracy to within a centigram is required. For coarser weighings an ordinary set of scales should be employed.
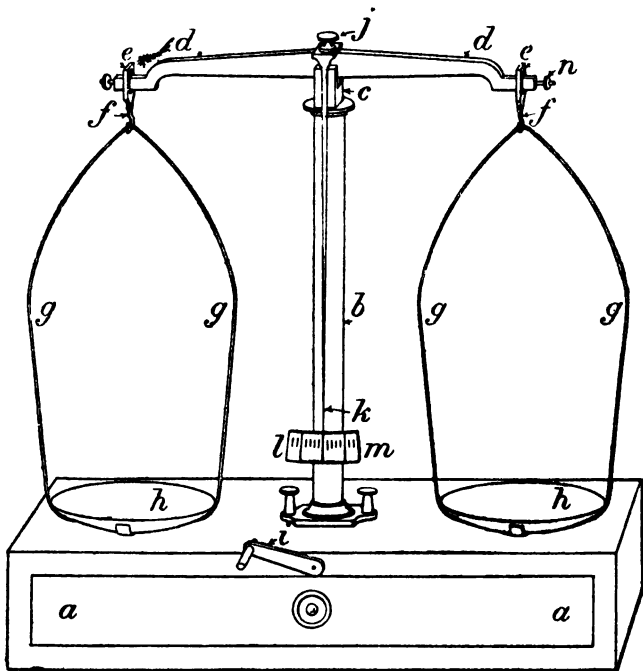
Fig. 8.—Delicate weighing balance.

In Fig. 8 a useful form of balance for laboratory work is shown. A very convenient size is one carrying a maximum weight of 250 grams, and turning with 1 milligram. The balance is carried on the mahogany box *a a*, in which is a drawer that may be used for weights and other weighing appliances. A brass pillar, *b*, is screwed to the top of the box, and supports, in a cradle, *c*, at the top, the central knife edges of the beam *d d*. On the ends of the beam, at *e e*, are also fitted knife edges, on which hang the hooks *f f;* and from these are suspended the bows *g g*, in which are carried the pans *h h*. In the centre of the front of the base of the balance is fixed a handle, *i ;* in the position shown in the figure, the pans are at rest on the balance base. But on turning this handle over to the right, the whole of the balance is raised by means of an eccentric, which actuates a sliding rod within the pillar *b*, and lifts the cradle *c*. The pans are then free to swing, and their motion is shown by the index-finger *j k*, which is screwed to the centre of the beam. The point of this index-finger vibrates in front of a graduated scale, *l m*, which has a long zero line in the centre. Prior to being used the balance should be set level, and the index-finger should be exactly in front of the centre of the scale. On raising the pans, by turning the handle *i*, the index-finger should vibrate an equal number of degrees each side of the central zero. Should it not do so, one of the pans is slightly the heavier, probably through not being quite clean ; in this case dust the whole balance carefully, and again test. If still out, the balance requires adjusting, which is done by means of the brass screw-nut *n* at the end of the beam. If the left-hand pan be too heavy, the nut must be screwed outward from the centre of the beam ; and in the contrary direction if the right-hand pan be the heavier. In a laboratory where several persons may be using the same balance, any adjustments should only be made by the teacher or demonstrator in charge. It is convenient to have more than one of these balances, in which case the larger may have a capacity of 500 or 1000 grams, and turn to a centigram ; while a second may be provided with a capacity of 50 grams, and turning with half a milligram. This latter should be enclosed in a glass case with sliding doors.

Weights.—These are generally arranged in a mahogany box, with a separate compartment for each weight, as shown in

Fig. 9. The larger weights are of brass, and range from a gram upwards. The smaller are usually constructed of aluminium, and are covered over with a glass lid, *a b.* For the purpose of lifting the weights the forceps *d* is provided; this has its place
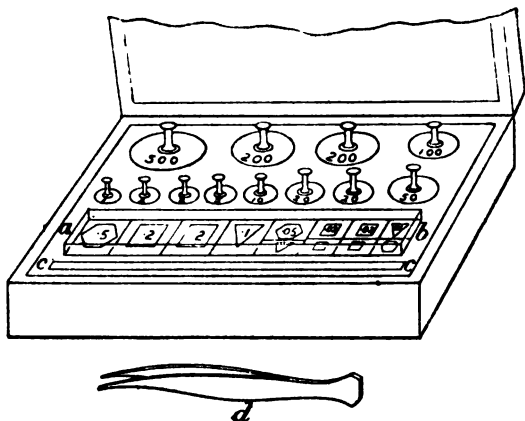
Fig. 9.—Box of delicate weights.

in the box *c c.* **Accurate weights such as these must on no account be touched with the fingers, but always lifted with the forceps.** The order in which the weights are placed in the box varies with different makes ; but the following is a frequent and convenient arrangement for a set of from 500 grams to 0·001 grams—

	500			200		200		100
	1	2	2	5	10	20	20	50
0·5	0·2	0·2	0·1		0·05	0·02	0·02	0·01
					0·001	0·002	0·002	0·005

The student will require to learn not only the denomination of each weight, but also its place in the box. He must be quite as well able to read the weights he has placed in the balance pan from the empty spaces as from the weights themselves.

Method of Weighing.—Let us suppose that it is necessary to weigh some piece of apparatus, as, for example, the glass

flask used in Exp. 2. This, in the first place, must be thoroughly cleaned and dried, and then placed on the left-hand pan of the balance. (As a matter of fact, the glass flask may very possibly have to be suspended from the balance hook at *f* by means of a piece of wire; this must be weighed with the flask.) Let the weight of the flask, or other piece of apparatus, be 238·847 grams; let us see how these figures are obtained. First, with the balance at rest, place the apparatus in position. Then take the 200-gram weight from the box by means of the forceps and place it on the right-hand pan; lift the balance by turning the handle *i* to the right, and notice which pan is the heavier; lower the balance by re-turning the handle. In this case the weight will not be sufficient, and the index-finger will swing to the right. Put in addition the 100-gram weight on the pan, and again raise the balance—the weight is too much, and the index-finger swings to the left. Do not forget that every time before a weight is added or removed the beam must be brought to a position of rest, this being done gently and carefully. Take out the 100 gram and try 50—too much; remove the 50 and try 20—not sufficient; add another 20—too much; remove the 20 and add 10—not enough; add 5—not enough; add 2—not enough; add another 2—too much; remove the 2 and add 1—not enough. As the weights get nearer and nearer to that of the flask the beam swings more and more slowly. Having now got at a point at which another gram more than turns the scale, commence in the same way with the fractions of a gram. Try first 0·5 gram—not enough; add 0·2—not enough; add another 0·2—too much; remove the 0·2 and try 0·1—not enough. At this stage the beam swings very slowly; it is best to start it, if necessary, by wafting a current of air down on one of the pans with the hand, until the index-finger swings very nearly to the extremity of the scale. Try next the 0·05-gram weight; the index-finger swings perhaps just six divisions to the left and five to the right—the weight is too much; remove the 0·05 and try 0·02—not enough; add another 0·02—not enough. Next add 0·005—not enough; but most likely the index-finger swings only a fraction of a degree further to the right than the left. Add 0·002—the index-finger swings the same number of degrees each side of the zero. The weights now exactly balance the flask. We must next read the weights; this must first be done from the box, reading the empty spaces.

In this case, we first have $200 + 20 + 10 + 5 + 2 + 1 = 238$. Against "weight of flask" write this number in the note-book. Next read off the decigram weight-spaces; there are empty, $0.5 + 0.2 + 0.1 = 0.8$. Write " $.8$ " after 238. The centigrams come next; they are $0.02 + 0.02 = 0.04$. Write " 4 " after 238·8· The milligrams are read in the same manner, and are $0.005 + 0.002 = 0.007$. Write " 7 " after the 238·84. The whole figure will then read—

"Weight of flask = 238·847 grams."

Having thus read the weight from the empty spaces in the box, next take out the weights and check off the reading as they are returned to their places. This double reading greatly reduces the chances of error in recording the weight of the substance. This operation of weighing has been described at full length, because it is the foundation of all exact chemical work ; these operations are, however, much shorter in practice than they appear on paper.

Remember in every case to use the greatest care when working with a balance ; never touch the weights with the fingers, nor leave them about out of their proper place in the box ; on the contrary, take every precaution to see that they are not soiled or otherwise injured.

CHAPTER II.

13. Modes of Chemical Action.—Although chemical actions vary so much in their character, they can all be classified under the following five heads :—

I. Direct Union or Synthesis.—Several experiments already performed belong to this class, as heating together copper and sulphur; many other examples will occur to the student as his knowledge of chemistry increases. The combination of hydrogen with chlorine or oxygen, producing hydrochloric acid and water respectively, are striking instances. Directions for the performance of these experiments are given in the chapters on the respective gases.

Experiment 13.—Place a small piece of phosphorus on an iron plate and drop on it a very little powdered iodine. Combination at once occurs, iodine of phosphorus being formed; the heat evolved inflames the phosphorus, which continues burning.

II. Chemical Displacement. — The various elements possess different degrees of chemical activity; thus, magnesium enters into combination with other elements with great readiness, as was shown by its brilliant burning when heated in the form of wire. Platinum, on the other hand, is almost inactive, and forms but very few compounds. In consequence of such differences in activity some elements are able to displace others from compounds already formed.

Thus iron is a more active element than copper, and if a piece of iron be placed in a solution of a compound of copper and chlorine, the iron displaces the copper; a compound of iron and chlorine is formed, and copper is liberated in the free state. Again, chlorine is a more active element than oxygen, and if water, a compound of oxygen and hydrogen, be submitted to the action of chlorine, the latter element displaces the oxygen, and a compound of chlorine and hydrogen is formed.

Experiment 14.—In a solution of chloride or sulphate of copper, acidulated with a few drops of hydrochloric acid, place a bright iron rod ; on removing it after a few seconds it will be seen to be coated with metallic copper, which has been displaced from its combination with the chlorine, chloride of iron being formed.

The chemical change may be thus represented :—

$$\begin{matrix} \text{Chloride} \\ \text{of copper} \end{matrix} \begin{cases} \text{Copper} \\ \text{Chlorine} \end{cases} = \begin{matrix} \text{Iron} \\ \text{Chlorine} \end{matrix} \begin{cases} \text{Chloride} \\ \text{of iron} \end{cases}$$
$$\qquad\quad \text{Iron} \qquad\quad \text{Copper}$$
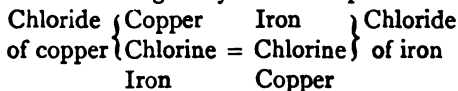
III. Mutual Exchange.—When two or more compounds are brought together, there are sometimes conditions which lead to an exchange between them of their various constituent elements. Thus, if solutions of mercury chloride (a compound of mercury and chlorine) and potassium iodide (a compound of potassium and iodine) be mixed together, the mercury and iodine, through mutual attraction, unite to form a new compound—mercury iodide. So, too, the remaining elements, potassium and chlorine, also unite to form a new compound—potassium chloride. Putting it in other words, the mercury has, under these conditions, a greater attraction for iodine than for chlorine, and consequently the mercury takes the iodine, and hands over the chlorine to the potassium.

Experiment 15.—Place in a test-tube some solution of perchloride of mercury and add to it, drop by drop, iodide of

potassium solution; a red powder is formed, which, from being suspended in the liquid, gradually falls to the bottom. This powder is iodide of mercury. Chloride of potassium remains in solution.

The chemical change may be thus represented:—

Chloride { Mercury ——————Mercury } Iodide of
of mercury { Chlorine   Iodine   } mercury.
Iodide of { Potassium   Potassium } Chloride of
potassium { Iodine   Chlorine } potassium.
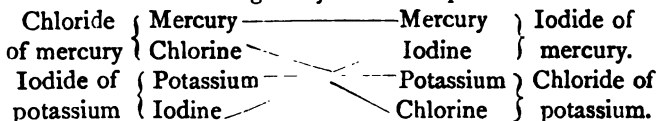
If in this experiment an excess of iodide of potassium be used, it re-dissolves the iodide of mercury. Whenever a substance separates from a solution through the addition of another body, as the iodide of mercury has done in this instance, the term *precipitate* is applied to the separated body.

IV. Re-arrangement of Particles.—This class of chemical action belongs almost exclusively to the domain of organic chemistry. There are many examples of compounds in which, without altering the proportions of each element present, fresh compounds may be formed by changing the arrangement of the particles within the compound. Such changes may be compared to those in which the same letters by transposition may be caused to form two distinct words.

V. Direct Decomposition.—The resolution of oxide of mercury into mercury and oxygen is an instance of this type of chemical action, which has already been described. The electrolysis, or separation by electricity, of water into its component elements is another example with which the student will shortly become acquainted.

14. Contact necessary for Chemical Action.— The whole of the various modes of chemical action are combination, decomposition, or interchange of particles of matter; from the very nature of such changes it is necessary that the bodies participating be in actual contact. Thus,

we know that, under the influence of heat, copper and sulphur combine, with vigorous chemical action; but if they are separated by an interval of space, combination is obviously impossible. Of necessity, then, we lay down the law that **chemical action can only occur between bodies actually in contact.**

Experiment 16.—Powder and mix together one part of loaf sugar and two of potassium chlorate. Take about as much of the mixture as can be held on a shilling and place on a stone slab. Dip the end of a glass rod in concentrated sulphuric acid; bring the rod as close to the mixture as possible, but not touching; notice that until actual contact ensues no action whatever occurs; the moment that they touch the whole mixture is inflamed.

In order that chemical action once commenced shall continue, it is necessary that means be provided for removing the products of such action as rapidly as formed, so that fresh portions of the substances may be brought into contact. The requisite mobility of particles necessary for this is best obtained by having one at least of the bodies in the liquid state. Either the bodies may, for this purpose, be dissolved in some suitable medium, or they may be liquefied by fusion.

Experiment 17.—Mix together some dry carbonate of soda and tartaric acid; no action whatever occurs. Place the mixture in a test-tube and add water; the substances are dissolved, and immediately a brisk effervescence ensues through the acid liberating carbon dioxide from the carbonate. Here chemical action is the result of the more intimate contact resulting from solution.

Experiment 18.—Mix together three parts by weight of nitre, two of dry carbonate of potash, and one of sulphur. Take a pinch *and no more* of this powder, and place in a small iron dish or ladle. Apply a gentle heat; as soon as the mixture is fused it detonates violently. The face should not be held near this substance when being heated. The powder ready mixed

is generally found in a laboratory. These substances may be preserved together in the solid state for an indefinite length of time, but combination immediately follows fusion.

In the matter of contact, chemical action apparently differs from heat and electricity as examples of other natural forces. Thus heat acts over great distances, as when the sun imparts heat to bodies on the earth; a glowing mass of red-hot iron will melt and inflame a piece of phosphorus placed some inches from it. So, too, an electrified glass rod attracts a pith ball held a considerable distance away.

Experiment 19.—Hold a red-hot iron bar some inches from a piece of phosphorus about the size of a pea. Observe that the heat travels over the intervening space and the phosphorus is inflamed, *i.e.* takes fire. (In this and similar experiments the phosphorus, or other inflammable material, should be placed on a piece of iron or other substance which will prevent the heat injuring the work-bench.)

Experiment 20.—Electrify a piece of ebonite or a rod of shellac by rubbing with warm flannel, hold it near some fragments of paper or other light objects; they are attracted. If wished, a piece of glass rod or tube may be rubbed with silk, and used instead of the ebonite and flannel; when the same effect is produced. Place a magnet near a suspended magnetic needle: notice that the one end is attracted and the other repelled, though the two may be six or more inches apart.

The difference, however, is apparent rather than real, for these forces only act at a distance by means of a medium which fills the space between the two objects, and thus produces continuity. The pull of a steam-engine may act on a mass of matter at some distance, because they are connected by a rope. Between the sun and the earth there is a medium by which the force of heat acts, which is just as real, though not so tangible, as the rope between a steam-engine and the bucket of ore it may be raising from the depths of a mine.

D

15. Heat Measurements.—Chemical action and heat are so materially dependent on each other that it becomes necessary for the chemical student to be familiar with the most important measures of heat.

16. Temperature.—The commonest heat-measure we have is that which we gain by means of the sensation of warmth it produces. According to the character of this sensation a body is said to be cold, warm, or hot. These terms all refer to the power which the body has of communicating heat to other bodies. The measure of this power is termed temperature, which is more exactly embodied in the following definition : **The temperature of a body is a measure of the intensity of its heat, and is further defined as the thermal state of a body considered with reference to its power of communicating heat to other bodies.**

17. The Thermometer.—For scientific purposes the sensations are not sufficiently accurate methods of measuring temperature ; accordingly temperature is usually measured by certain of the effects which heat produces. Among these one of the most convenient is that most bodies expand with an elevation of temperature. This expansion is distinctly perceptible with solids, occurs to a greater extent in liquids, and most of all with gases. For the general purposes of temperature-measurement, the metal mercury is the most convenient substance. This liquid, enclosed in a suitable vessel, constitutes the temperature-measuring instrument termed a thermometer. In constructing a thermometer, a bulb is blown at one end of a glass tube of very narrow bore ; the bulb and a portion of this tube are next filled with carefully purified mercury ; this is boiled, and thus all air and moisture are driven out of the tube ; the open end is then hermetically sealed by fusing the glass itself. One then has the bulb and a portion of the tube filled with mercury, and the remainder of the tube a vacuum, save for the

presence of a minute quantity of mercury vapour. On heating the bulb of this instrument the mercury expands and rises considerably in the stem. Throughout any body or series of bodies, heat has a tendency to so distribute itself that the whole series shall be at the same temperature; consequently if the thermometer be placed in contact with the body whose temperature it is desired to measure, a redistribution of heat occurs, until the two are at the same temperature. That is to say, if the body be the hotter it receives heat from the thermometer, and if it be colder it yields heat to the thermometer, until the temperature of the two is the same. The two being in efficient contact, this stage is indicated by the mercury becoming stationary in the thermometer. Now the volume of mercury is constant for any one temperature; therefore, to register temperature, it is only necessary to have further a scale or series of graduations attached to the stem of the instrument, by which the temperature may always be read.

8. Thermometric Scales.—In graduating thermometers, two fixed points of temperature are almost universally employed: these are the temperatures of melting ice, and of the steam from boiling water. Certain simple precautions being taken, these temperatures are always constant. It is, in addition, necessary to graduate the thermometers, so as to register temperatures intermediate between these two points, and also below and above them. The most convenient system of graduation is that of Celsius, known also as the Centigrade scale. In this scale the distance between the melting-point of ice (or the freezing-point of water, as it is commonly termed) and the temperature of steam at ordinary pressure is divided into 100 equal graduations or degrees. (This latter temperature is more commonly described as being that of the boiling-point of water.) The freezing-point is called zero, or 0°, and the boiling-point 100°. Degrees of the same value are

set out above and below the boiling and freezing points :
the temperatures below o° are reckoned in − degrees,
counting downwards; thus 10° below the freezing-point is
− 10°, and so on.   Degrees above the boiling-point simply
count upwards; thus 10° above the boiling-point is 110°,
and so on, to as high temperatures as have been measured.
This scale is exceedingly convenient, and is that most
largely used by scientific men in all countries; it is also
the scale adopted for general use in France.   In England
the scale known as that of Fahrenheit is commonly adopted :
the distance between the freezing and boiling points is
divided into 180 equal parts, and degrees of the same
dimensions set out above and below the boiling and
freezing points.   Fahrenheit assumed that the greatest cold
attainable was 32° below the freezing-point, and accordingly
took that point as his zero and reckoned from it upwards.
The freezing-point thus became 32° F., and the boiling-
point 32 + 180 = 212° F.   Degrees below the Fahrenheit
zero reckon downwards as minus degrees.   In Germany and
Russia temperature is reckoned on the Réamur scale, in
which the freezing-point is o° and the boiling-point 80°.   It
is frequently necessary to be able to compare these scales,
and to translate temperatures from any one into another.
The following comparative values of the degrees of each
scale will be of assistance to the student in doing this :—

1 Centigrade degree .	.	$= \frac{9}{5}$ Fahrenheit degree.
1 „ „ .	.	$= \frac{4}{5}$ Réamur „
1 Fahrenheit „	.	$= \frac{5}{9}$ Centigrade „
1 „ „	.	$= \frac{4}{9}$ Réamur „
1 Réamur „ .	.	$= \frac{5}{4}$ Centigrade „
1 „ „ .	.	$= \frac{9}{4}$ Fahrenheit „

Conversions from Centigrade to Réamur, and *vice versâ*, are
very simple, because the zero of the two scales coincide.
So, too, it is easy to convert any number of degrees
Centigrade into the equivalent number of Fahrenheit degrees
above the freezing-point; but after this is done, provision

must be made for the difference of the zeros. The same holds good for the converse operation. The following formulæ show how temperatures on the one scale may be converted into those of another :—

$$\text{Centigrade to Fahrenheit} \qquad \frac{C.° \times 9}{5} + 32 = F.°$$

$$\text{,, \quad ,, Réamur} \qquad \frac{C.° \times 4}{5} = R.°$$

$$\text{Fahrenheit to Centigrade} \qquad \frac{(F.° - 32) \times 5}{9} = C.°$$

$$\text{,, \quad ,, Réamur} \qquad \frac{(F.° - 32) \times 4}{9} = R.°$$

$$\text{Réamur \quad ,, Centigrade} \qquad \frac{R.° \times 5}{4} = C.°$$

$$\text{,, \quad ,, Fahrenheit} \qquad \frac{R.° \times 9}{4} + 32 = F.°$$

19. Quantity of Heat. — Temperature is not a measure of quantity of heat, for a thermometer would indicate the same temperature both in a vessel containing a pint, and one containing a gallon, of boiling water, although it is evident that the one must contain eight times as much heat as the other; further, to raise the gallon of water to the boiling-point, eight times the amount of heat necessary to similarly raise the pint is required. This leads us to the mode of measuring and indicating *quantity* of heat. **Quantity of heat is measured by the amount necessary to raise a certain weight of some body from one to another fixed temperature. The quantity of heat necessary to raise 1 gram of water from 0° to 1° C. is termed a Unit of Heat.**

20. Absolute Temperature. — There are certain reasons which lead us to suppose that at a temperature of — 273° C. bodies would be entirely devoid of heat. This point — 273° C. is therefore often termed the absolute zero of temperature, and temperature reckoned therefrom is

termed " absolute temperature." The absolute temperature of a body is its temperature in degrees C. + 273.

21. Expansion and Contraction of Gases.—All gases expand with increase, and contract with diminution, of temperature. The amount of expansion and contraction is the same for all gases between the same limits of tempe‐ rature, provided the temperature is considerably higher than that at which they condense to liquids. **The volume of all gases is directly proportional to their absolute tempe‐ rature.** Because of this variation with temperature it is **necessary to fix a temperature which shall be considered as a standard in expressing the volume of a gas: 0° C. is commonly adopted for this purpose.**

Knowing the volume of a gas at any one temperature, its volume at any other may be easily calculated ; thus, a vessel was found to contain 750 c.c. of air at 15° C.; it is required to find its volume at the standard temperature :—

$$15° \text{ C.} + 273 = 288° \text{ absolute temperature.}$$
$$0° \text{ C.} + 273 = 273° \qquad \text{,,}$$

As 288 : 273 :: 750 : 611 c.c. of gas at standard tempera‐ ture.

The volume of a gas is also affected by the pressure to which it is subjected : this variation is governed by what is called Boyle and Marriotte's law. **The volume of any gas is inversely proportional to the pressure to which it is subjected.** This law also only holds good in strictness when the temperature of the gas is considerably above the liquefying-point. The most important variations of pressure to which gases are liable are those resulting from the changes in pressure of the atmosphere. The height of the mercury column of the barometer is a direct measure of the pressure of the atmosphere ; therefore that pressure is commonly expressed in the number of millimetres (m.m.) which that column is high. **For purposes of comparison it is also** ·necessary to reduce all pressures to one standard ; that

selected is an atmospheric pressure which causes the barometer to stand at 760 millimetres.

As an example of a calculation of the volume of a gas when the pressure is varied, the following may be taken : 1000 c.c. of gas is measured at a pressure of 750 m.m. ; required its volume at the standard pressure of 760 m.m. :—

As 760 : 750 :: 1000 : 987 c.c. of gas at standard pressure.

The temperature and pressure quoted as standards for gas measurement, o° C. and 760 m.m., are often termed **normal temperature and pressure** : for this expression, the abbreviation ' N.T.P.' is frequently used.

Finally, the student is specially requested to bear in mind that, when sufficiently far removed from their liquefying-points, **all gases expand and contract equally for similar variations in temperature and pressure, their behaviour in this respect being independent of their chemical properties.**

22. Chemical Separations.—The chemist frequently finds, in the course of experiment, that it is necessary to separate bodies from each other ; the processes employed for this purpose are varied, depending on the nature of the substances. As in many future operations it will be necessary to use one or more of them, it is advisable that at this stage they should be studied. There is, as a rule, some particular property which one of the elements or compounds in a mixture possesses which the other does not : thus one may be soluble in water, the other insoluble ; this at once affords a means of separating them. **The principal methods of separation employed are Solution, Decantation, Filtration, Crystallization, Evaporation, Distillation, Sublimation, and Ignition.**

23. Solution, Decantation, and Evaporation. —A mixture of two bodies, one only of which is soluble in water, is separated by the action of that solvent.

Experiment 21.—Take some of a mixture of sand and salt, place in a test-tube, add water, and shake up; allow the sand to subside; the clear solution on the top is to be carefully poured off, without disturbing the sediment, into an evaporating-basin. The process is known as *decantation.* Place a piece of wire gauze on one of the rings of the retort stand, adjusted at a suitable height above the Bunsen burner; put the evaporating-basin containing the solution of salt on the gauze and light the burner, keeping the flame small; the water will gradually evaporate, and crystals of salt will form. The object of placing the wire gauze under the basin is to prevent the flame coming in actual contact with and cracking it. The water has been driven off by *evaporation.*

In cases where both bodies are insoluble in water, some substance must be selected which acts on the one without the other.

Experiment 22.—Place some of a mixture of sand and marble in a test-tube, add some distilled water, and heat. Take out a few drops of the water, and evaporate them on clean platinum foil; they entirely disappear, or only leave the slightest stain on the foil. This is the usual test employed to ascertain whether a solvent has dissolved anything or not. Decant off the water and add dilute hydrochloric acid to the mixture; effervescence occurs. When this is over, again take out a few drops of the liquid and evaporate on the foil; a considerable residue will remain. The best plan to get a few drops out of a test-tube is to put in the end of a glass tube; then close the top with the finger, and withdraw it. On removing the finger the small portion it contains runs out.

The separation in this experiment depends on the fact that chalk is dissolved by hydrochloric acid, while sand is not affected by it.

24. Filtration.—There are many cases in which decantation is not suitable for the purpose of separating a liquid and solid; the solid body may perhaps be so finely divided that it remains suspended in the liquid, giving it

a muddy appearance. Under these circumstances, *filtration* is resorted to.
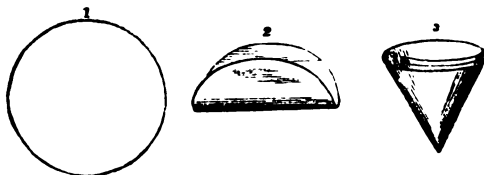
FIG. 10.—Folding filter paper.

Experiment 23.—Take a filter paper about 3½ inches diameter, and double it twice ; then open it into a cone, taking three folds of paper on the one side and one on the other, as shown in Fig. 10. Place this cone of paper in a glass funnel, which it will just fit, and moisten with water. Care must be taken that the point of the folded filter does not get broken. Next add to a solution of calcium chloride some ammonium carbonate ; a white precipitate is formed. Pour the whole on the filter, holding a glass rod against the lip of the beaker or testtube down which the liquid runs (Fig. 11) ; the clear liquid known as the filtrate passes through, and must be collected in a beaker ; the precipitate, consisting of calcium carbonate,

FIG. 11.—Filtration.

remains on the filter. Pour some clean water on it for the purpose of washing. After this has drained off, remove the beaker, push a hole through the bottom of the filter, wash the precipitate into an evaporating-basin, and dry it. The filtrate contains ammonium chloride, which may be obtained by evaporation.

25. Crystallization.—Where two bodies are mixed together, both of which are soluble in water, but in different degrees, another plan may be adopted for their separation.

Experiment 24.—Take a mixture of about equal parts of potassium chlorate and potassium chloride. Place some in a test-tube, and add just sufficient water to dissolve the whole on boiling ; now allow the solution to cool ; tabular crystals will separate out, consisting of the less soluble potassium chlorate. When cold, filter these off, just wash with cold water, and dry at a gentle heat.

Separation by crystallization is a process largely used for manufacturing purposes.

26. Distillation.—In the experiments made by evaporation, we have only as yet dealt with the solids which remain, but in many cases the liquid is also required. In the laboratory, where pure water is an essential, it is obtained by this process of distillation, in which the steam is again condensed and collected.

Experiment 25.—Take either an ordinary flask fitted with
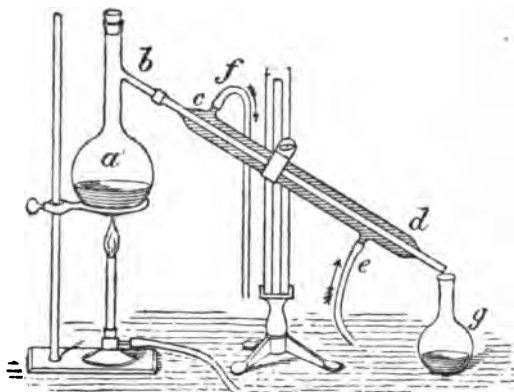
Fig. 12.—Apparatus arranged for distillation.

cork and delivery tube, or, preferably, a flask with side tube, *a b*, as shown in Fig. 12. Half fill it with brine, to which a few

drops of colouring matter (red or black ink will do) have been added ; fix it in the retort stand, and connect the tube *b*, as shown, by a cork to a Liebig's condenser, *c d.* The condenser consists of two glass tubes, one fitting inside the other ; the steam passes through the inner one, and, as condensed, runs into the flask, *g*, placed as a receiver. Through the outer tube a current of cold water is passed, which speedily condenses the steam. The pipe *e*, conveying the water, is attached to the lower end of the condenser by means of the pipe *f;* the overflow water is led to a drain. After some water has collected in the receiver, taste it, and notice that it is perfectly free from salt and also colouring matter.

27. Sublimation.—This is a process somewhat analogous to distillation ; it is, in fact, distillation of substances which condense in the solid instead of the liquid state.

Experiment 26.—Heat a small portion of a mixture of sand and ammonium chloride in a test-tube ; dense white fumes are evolved, which condense as a white crust in the upper part of the tube, the sand remaining behind.

Bodies which distil or sublime are termed *volatile*, and those which neither distil nor sublime are said to be *fixed.*

28. Ignition.—Occasionally the chemist avails himself of the combustibility of bodies, and burns them off from others which are incombustible.

Experiment 27.—Place some of a mixture of sand and lampblack or soot on platinum foil, and keep at a bright red heat for some time with the Bunsen ; the lampblack will burn off, leaving the incombustible sand behind. It may be mentioned that when directions are given to *ignite* a body, it simply means that it is to be heated intensely ; it does not follow that it will burn.

Summary.

Modes of chemical action :—
    I. Direct union.
   II. Chemical displacement.
 III. Mutual exchange.
 IV. Re-arrangement of particles.
  V. Direct decomposition.

Contact is necessary for chemical action, while heat, light, etc., apparently act over considerable distances.   Liquidity of the participating bodies aids chemical action.

Chemical action and heat are closely related.   Various heat-measurements, temperature.   The thermometer, conversion of thermometric scales.   Quantity of heat.   Absolute temperature. Laws of expansion and contraction of gases.

Methods of separation employed by the chemist : solution, decantation, filtration, crystallization, evaporation, distillation, sublimation, and ignition.

OBJECT DEMONSTRATION.

Note carefully the appearance and properties of the different substances used in the various experiments.

Phosphorus is a waxy-looking solid, which has to be kept under water because of its inflammability.   It gives off smoke when exposed to the air, and is faintly luminous in the dark.

Iodine is a bluish-black powder with peculiar odour.

Note that concentrated sulphuric acid is a heavy colourless liquid.   Observe carefully the manner in which a filter is folded, and satisfy yourself that the liquid cannot run out except through the pores of the paper.   In filtering, observe how the liquid runs down the rod used, also that by capillary attraction it creeps up the sides of the folded filter.

Examine carefully the general arrangement and fitting up of the distillation apparatus in Fig. 12.   Notice how the different joints are made air-tight, also direction in which water passes through the condenser, and how the glass body *c d* is held in the condenser stand.

LABORATORY DIRECTIONS.

Great care must be taken in the handling of phosphorus ; it is always kept under water because of its inflammability.   If a small piece is wanted, take a stick out of the bottle with a pair of tongs, place it under water, and cut it while there.   Dry it by pressing gently between folds of filter paper or a duster.   It should not be touched with the fingers.

The student should not forget that sand and solid substances generally should *never* be thrown down the drains, but put into a box or other receptacle specially provided.

CHAPTER III.

29. List of Elements. — Although the number of different substances observed around us is practically infinite, yet there are comparatively few elements. Practically, all natural bodies are mixtures either of elements or compounds ; in many of the mixtures, however, one element or compound largely predominates, while in a few cases the element or compound is found in a condition of almost absolute purity. On investigation these natural mixtures and compounds are found to be capable of resolution into elements, and although the compounds are so diverse in character, yet it is estimated that nine hundred and ninety-seven thousandths of the earth's crust is composed of only nine elements. In addition to these nine very plentiful elements, there are about thirty that may be termed common, while the remainder of the list, given in the subjoined table, are rare or very rare. It should be noticed that our definition of an element is a somewhat tentative one ; it is not said that an element is a body which *cannot* be separated into dissimilar substances, but a body which *has not*. The accepted list of elements has undergone some curious vicissitudes. With the advance of chemical science certain bodies at one time supposed to be elements have been discovered to be compounds, and as more substances have been subjected to chemical research and by far more refined and powerful modes of examination, a number of elements existing in only minute quantities have been added to the list.

The following table contains a list of the known elements, their symbols, atomicities, or valencies, where known, and combining or atomic weights. The combining weights given are those derived from the experiments of Stas. For most calculations the nearest whole number or whole number with ·5 may be employed. Thus chlorine may be taken as 35·5, oxygen as 16, and so on.

Name.	Symbol.	Atomicity or valency.	Combining or atomic weight.
Aluminium . . .	Al	IV	27·3
Antimony (stibium)	Sb	V	132·0
Arsenic	As	V	74·9
Barium	Ba	II	136·8
Beryllium .	Be		9·0
Bismuth . .	Bi	V	210·0
BORON	B	III	11·0
BROMINE . . .	Br	I	79·75
Cadmium . . .	Cd	II	111·6
Cæsium . . .	Cs	I	133·0
Calcium . . .	Ca	II	39·9
CARBON . . .	C	IV	11·97
Cerium . . .	Ce		141·2
CHLORINE . . .	Cl	I	35·37
Chromium . . .	Cr	VI	52·4
Cobalt	Co	IV	58·6
Copper (cuprum) .	Cu	II	63·0
Didymium . .	D		147·0
Erbium . . .	E		169·0
FLUORINE . . .	F	I	19·1
Gallium . . .	G		69·8
Gold (aurum) . .	Au	III	196·2
HYDROGEN . .	H	I	1·0
Indium . . .	In	III	113·4
IODINE	I	I	126·53
Iridium . . .	Ir	IV	196·7
Iron (ferrum) . .	Fe	VI	55·9
Lanthanum . .	La		139·0
Lead (plumbum) .	Pb	IV	206·4
Lithium . . .	Li	I	7·01

Name.	Symbol.	Atomicity or valency.	Combining or atomic weight.
Magnesium . . .	Mg	II	23·94
Manganese . . .	Mn	VI	54·8
Mercury (hydrargyrum)	Hg	II	199·8
Molybdenum . . .	Mo	VI	95·6
Nickel	Ni	IV	58·6
Niobium . . .	Nb	V	94·0
NITROGEN . . .	N	V	14·01
Osmium . . .	Os	VI	198·6
OXYGEN . . .	O	II	15·96
Palladium . . .	Pd	IV	106·2
PHOSPHORUS . .	P	V	30·96
Platinum . . .	Pt	IV	196·7
Potassium (kalium) .	K	I	39·04
Rhodium . . .	Rh	IV	104·1
Rubidium . . .	Rb	I	85·2
Ruthenium . . .	Ru	VI	103·5
SELENIUM . . .	Se	VI	78·0
Silver (argentum) . .	Ag	I	·107·66
SILICON . . .	Si	IV	28·0
Sodium (natrium) .	Na	I	22·99
Strontium . . .	Sr	II	87·2
SULPHUR . . .	S	VI	31·98
Tantalum . . .	Ta	V	182·0
TELLURIUM . . .	Te	VI	128·0
Thallium . . .	Tl	III	203·6
Thorium . . .	Th		231·5
Tin (stannum) . .	Sn	IV	117·8
Titanium . . .	Ti	IV	48·0
Tungsten . . .	W	VI	184·0
Uranium . . .	U	VI	240·0
Vanadium . . .	V	V	51·2
Yttrium . . .	Y		93·0
Zinc	Zn	II	64·9
Zirconium . . .	Zr	IV	90·0

30. Metals and Non-Metals.—The elements have been divided into two groups, according to whether they are metallic or non-metallic in their nature. The metallic properties are very decided in a metal such as either iron,

copper, or gold ; and equally it is obvious that such bodies
as sulphur and phosphorus are not metals.   But although
the properties of these are very definite, a number of other
bodies are much less marked in character ; in fact, there is
no well-defined line of division between the two classes, as
the one series gradually merges into the other.   Thus the
element arsenic, which occupies an intermediate position,
is placed by some chemists among the metals, and by others
among the non-metals.   **In physical character the metals
are, in mass, opaque bodies, having a peculiar lustre
termed metallic ; they are comparatively good conductors
of heat and electricity.**   These properties do not exclusively
belong to the metals, for carbon in the form of graphite
has a very decided metallic lustre, and conducts electricity
well.   **Chemically, the metals as a whole form oxides
which act as bases, while the non-metallic oxides form
acids, but even in this respect the two series overlap each
other.**   (The meaning of the terms " oxide," " base,"
and " acid " is fully explained in subsequent chapters.)
The non-metals in the table just given · are indicated
by being printed in small capitals ; the common metals
are printed in ordinary type, and the rarer metals in
italics.

At ordinary temperatures two of the elements—mercury
and bromine—are liquid ; four—hydrogen, chlorine, oxygen,
and nitrogen—are gaseous, but can be liquefied by intense
cold and pressure.   The remaining elements are solid,
but at varying temperatures have been liquefied, with
the exception of carbon, which so far has only been
slightly softened with the highest temperatures at our
command.

31. Composition of the Earth's Crust. — From
analysis of various samples of rock and rock-forming
materials, it has been estimated that the earth's crust has
the following approximate composition :—

Oxygen	.	.	.	.	.	480
Silicon.	.	.	.	.	.	290
Aluminium	.	.	.	.	.	80
Iron	.	.	.	.	.	60
Calcium	.	.	.	.	.	30
Magnesium	.	.	.	.	.	20
Sodium	.	.	.	.	.	20
Potassium	.	.	.	.	.	15
Hydrogen	.	.	.	.	.	2
Other elements	.	.	.	.		3
						1000

32. **Symbols and Formulæ.**—For convenience of description **each element has an abbreviation of its full name, called its symbol.** These abbreviations consist, where practicable, of the initial letter of the Latin name of the element. As, however, there are nearly seventy elements, and only twenty-six letters in the alphabet, a large number of the symbols are composed of the initial and another distinctive letter selected from the name. Thus, the three elements carbon, chlorine, and copper (cuprum), all have names commencing with 'C;' carbon, being the most important element, has the letter C for its symbol, while Cl and Cu are written respectively for chlorine and copper. The symbols are given in the Table of Elements, contained in paragraph 29.

As all compound bodies are the result of the union of elements, they may be conveniently expressed symbolically by placing side by side the symbols of the constituent elements. **The symbol of a compound is termed its formula.** Thus common salt consists of sodium and chlorine, and NaCl is accordingly written for its formula.

33. **Further Uses of Symbols and Formulæ.**— Simply as abbreviations of the full names, symbols and formulæ are of great service ; this, however, is but a small part of their significance and value in chemistry. Much of their further use may best be explained when the students'

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experimental knowledge is further extended. Meanwhile, it is sufficient to state that in addition to its use as an abbreviated title of any element, the symbol represents the relative quantity of the element indicated by its combining weight, that of hydrogen being taken as unity. When compounds contain multiples of the combining weight of any element, the fact is indicated by placing a small figure after the symbol and slightly below the line. The large figures at times used before a symbol or formula apply to the whole of the symbol or formula which follows. The combining weights are given in the table of the elements in paragraph 29.

As previously stated, the formula of sodium chloride is NaCl, and it contains 23 of sodium to 35·5 of chlorine. The formula of hydrochloric acid is HCl, and it contains 1 of hydrogen to 35·5 parts of chlorine. Water consists of 2 parts of hydrogen to 16 of oxygen; the fact that it contains twice the combining weight of hydrogen is expressed by writing the formula H_2O. Again, ammonia contains 3 parts by weight of hydrogen to 14 parts of nitrogen; consequently it has the formula NH_3. The gas termed carbon dioxide consists of 32 parts, or twice the combining weight, of oxygen to 12 by weight of carbon; the formula is consequently CO_2. The quantity of an element represented by its combining weight is termed "one combining proportion" of that element. The relative weights of these "combining proportions" have been determined with the utmost possible exactitude, most careful analytic experiments having been made for that purpose. A description of some of these will subsequently be given.

34. Chemical Equations.— Chemical changes are most conveniently expressed by what are termed "chemical equations;" these consist of the symbols and formulæ of the bodies participating placed before the sign =, while those of the resulting bodies follow.

As an example, the following equation represents the

chemical action occurring when solutions of mercury chloride
and potassium iodide are mixed together.

$$HgCl_2 \quad + \quad 2KI \quad = \quad HgI_2 \quad + \quad 2KCL$$

<div align="center">
Mercury   Potassium   Mercury   Potassium
chloride.   iodide.   iodide.   chloride.
</div>
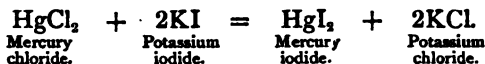
With the assistance of a table of atomic weights, the
chemist learns from this equation that one part of mercury
chloride, containing one combining proportion of mercury
weighing 200, and two combining proportions of chlorine,
each weighing 35·5, together with two parts of potassium
iodide, each containing one combining proportion of potas-
sium weighing 39, and one of iodine weighing 127, together
yield or produce one part of mercury iodide, containing one
combining proportion of mercury weighing 200, and two of
iodine each weighing 127, and two parts of potassium chloride,
each consisting of one combining proportion of potassium
weighing 39, and one of chlorine weighing 35·5. **As no
chemical change affects the weight of matter, the weight
of the quantity of a compound represented by its formula
must be the sum of those of the constituent elements ; so,
too, the weight of the bodies resulting from a chemical
change must be the same as that of the bodies before the
change, whatever it may be, had occurred.** Also the same
number of " combining proportions " of each element must
appear on each side of the equation. Although, given a
chemical equation and table of combining weights, it is
possible to state what relative weight of each element is
concerned in any chemical action, it must never be forgotten
that **such weights are always determined in the first
place by chemical analysis, and then the equation compiled
from the date thus obtained.** So, too, the series of com-
bining weights is simply a tabular expression of results
obtained by practical analytic investigation.

35. Atoms and Molecules.—The fact that the
quantity of every element which enters into combination is
either a certain definite and unchangeable weight, or a

multiple of that weight, has caused chemists to feel that this weight of a combining proportion of an element is in some way associated with its physical nature. This view is strengthened by the fact that throughout the whole series of known compounds each element invariably obeys this law. Chemists are therefore led to assume a unit of chemical combination, and to this they have given the name of "atom," a word which signifies that which is indivisible. For chemical purposes, **an atom may be defined as the unit quantity of chemical combination of each element, and is the smallest quantity of any element which has been caused to enter into, or to be expelled from, a chemical compound. For the phrase "combining proportion," the term "atom" may be substituted. The combining weight is thus the relative weight of the atom of each element compared with that of hydrogen, which, being the lightest, is taken as unity.**

The little group of atoms represented by the formula of a compound is termed a "molecule." **A molecule is the smallest possible particle of a substance which is capable of separate existence.** No subdivision of molecules of chemical compounds is possible without the decomposition of such compounds either into the atoms of the constituent elements, or into two or more molecules of some simpler chemical compound or compounds.

36. Elementary Molecules. — The definition just given of molecules applies not only to compounds, but also to elementary bodies. **The elements in the free or uncombined state exist in the form of molecules, such molecules in most cases consisting of two or more atoms united together.** The number of atoms present in the molecule of an element, is shown by a small figure after the symbol; thus a molecule of oxygen, containing two atoms, is represented by O_2. When in any case it is desired to express symbolically a number of atoms of an element, this must be done by the use of a large figure before the

symbol ; thus 2O or 8O means simply two or three atoms of oxygen, but O_2 or O_3 would mean that the molecule contained either two or three atoms of oxygen as the case might be.

The whole atomic and molecular theory will subsequently receive more ample description and explanation.

Summary.

Names, symbols, atomicity, and combining or atomic weights of the elements.

Division into metals and non-metals, into solids, liquids, and gases.

Approximate composition of the earth's crust. Symbols, formulæ, and equations.

Definitions of " atom " and " molecule."

OBJECT DEMONSTRATION.

Examine carefully specimens of as many as possible of the elements, noticing particularly the metallic character of the metals proper, such as silver, gold, and copper. Observe that antimony is very decidedly metallic in appearance, and that arsenic closely resembles it, while phosphorus is altogether devoid of metallic character ; although, chemically, these elements, in some particulars, are very closely allied to each other. Note that graphite, a non-metallic element, has a distinct metallic lustre ; likewise that iron pyrites, a natural compound (of iron and sulphur), has also a very bright metallic lustre. Observe the appearance and characters of the two liquid elements—mercury and bromine.

CHAPTER IV.

Oxygen.—Symbol, O. Atomic weight, 15·96. Density, 15·96. Specific gravity, 1·1056. Molecular formula and weight, O_2,31·92. Boiling-point, −130° C., under 475 atmosphere

The density of a gas is its weight, volume for volume, compared with hydrogen taken as unity ; the specific gravity is its weight compared with an equal volume of air. Molecular weight and volume are explained in Chapter IX.

37. Occurrence.—Oxygen occurs plentifully in nature, both in the free state and in combination with other elements. About one-fifth of the atmosphere consists of this gas ; it constitutes eight-ninths by weight of water, and, as shown in the table given on a previous page, about 48 per cent. of the earth's solid crust.

38. Discovery.—Dr. Priestley, of Birmingham, discovered, in 1774, that by heating mercury in contact with air in a closed vessel the volume of the air was lessened, and that red scales were formed on the surface of the mercury.

Experiment 28.—In order to repeat Priestley's experiment, the following apparatus may be used. Procure first a round-bottom glass flask, *a*, about 3 inches diameter, and with a very long neck, about half an inch internal diameter. Bend this neck as shown in Fig. 13, *b c d.* Procure also a mercury pneumatic

trough, *c f,* shown in the figure in section, and having a small supporting shelf, *g,* at the one end. This shelf is provided with a slot opening outward, through which the tube *c d* can easily pass. Fix the glass flask in a retort stand, *h i,* and support the mercury trough on blocks of wood, standing on the base of a second retort stand, *j k,* so that the flask tube takes the position shown in the figure. Take a gas-jar, *l m,* invert it over the end
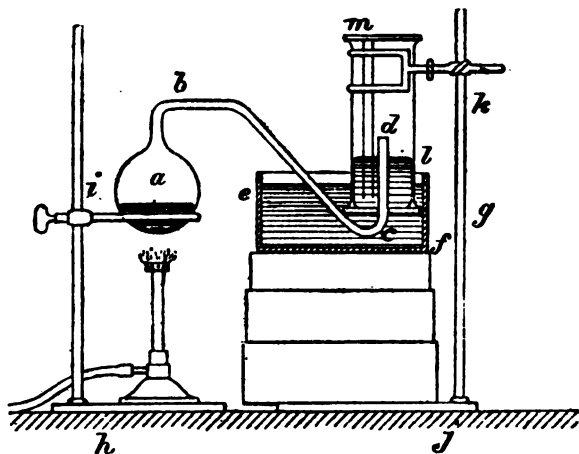
FIG. 13.—Absorption of oxygen from air by mercury.

of the tube *c d,* and stand it on the shelf *g.* Arrange the clamp *n* to hold the jar firmly in this position. Next fill the trough with mercury to the height shown in the figure; then unclamp the flask *a* from the retort stand ; shift it and the gas-jar *l m* to the centre of the trough. Holding one in each hand, practise withdrawing the end of tube *c d* from the flask *without permitting the mouth of the gas-jar to rise above the surface of the mercury.* (If necessary, the bends of the tube *b c d* must be readjusted to permit of this.) Next, having thoroughly cleaned and dried the flask *a,* pour into it about 8 oz. of mercury. Paste a narrow paper strip along the length of the gas-jar, about half fill it with mercury, and cover the top with a glass plate. Invert the jar, holding the plate firmly, and put its mouth below the surface of the mercury in the trough. Holding it there, insert the end of

the bent neck of the flask *a*, in which the mercury has previously been poured, and slide the gas-jar on to the shelf.   Clamp both flask *a* and gas-jar firmly in their proper positions by means of their respective retort stands.   *While thus connecting the flask and jar, the mouth of the latter must not be permitted to rise above the surface of the mercury in the trough.*   Having thus fixed the whole of the apparatus as shown in the figure, mark the exact height of the mercury in the gas-jar on the paper slip on the outside.   The mercury within the flask is now in contact with the air in the jar, but is shut off from the atmosphere.

Very gently heat the mercury in the flask by means of a Bunsen burner with a rose top, and maintain the temperature at a point just below the boiling-point of mercury for two or three days.   With the increased temperature the air first expands, and the mercury is depressed in the gas-jar ; but the original height must be so arranged that no air escapes from the jar with the heating of the flask.   At the end of that time allow the apparatus to cool.   The mercury rises in the gas-jar above its original height, thus showing that the air has suffered a diminution in volume.   Observe that red scales are floating on the mercury in the flask *a*.   Disconnect the flask, and carefully withdraw its mouth-tube from the gas-jar, taking care to keep the mouth below the surface of the mercury in the trough the whole time.   Stop the mouth of the gas-jar with a glass plate, remove it from the trough, and stand it on the table.   Slightly open the mouth of the jar, and plunge a previously lighted taper into the residual gas—the taper is extinguished.

The red scales produced consist of oxide of mercury. The chemical change may be thus represented :—

$$2Hg \quad + \quad O_2 \quad = \quad 2HgO.$$
$$\text{Mercury.} \qquad \text{Oxygen.} \qquad \text{Mercury oxide.}$$
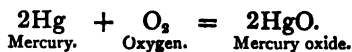
The experiment also shows that a gas has been withdrawn from the air ; and, further, that the gas which remains no longer supports combustion, as does the original air.

Many other metals—among which, for example, is copper—share with mercury this property of withdrawing oxygen from air, with the formation of an oxide of the metal.

39. Preparation.—The student is aware from Exp. 11 that oxide of mercury is decomposed into oxygen and mercury by a strong heat—

$$2HgO = 2Hg + O_2.$$
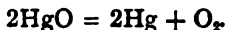
This experiment should be again repeated and the gas evolved collected. In practice, the oxide of mercury is prepared by other and more convenient methods than that employed by Priestley.

Before proceeding further prepare the apparatus for collection of gases, specified in the laboratory hints at the end of this chapter; also read the whole of the directions there given carefully through.

Experiment 29.—In gas apparatus No. 1 substitute one of the combustion tubes for an ordinary test-tube ; place in it about as much oxide of mercury as could be held on a sixpence ; clamp it in the retort stand, or hold by means of a test-tube holder in the hand (it is preferable to use the retort stand) ; arrange the pneumatic trough and a small gas-jar for the collection of gas, as shown in Fig. 14. The quantity of mercury oxide is much less than that of potassium chlorate mixture which is shown in the figure. Carefully heat the mercury oxide with the Bunsen burner, and observe the evolution of gas. When the jar is full, take it out of the trough and introduce a glowing splinter ; the rekindling shows that the gas is oxygen. A large test-tube may be used if a small gas-jar is not obtainable.

Most of the methods employed for the preparation of oxygen are instances of direct decomposition. The substance most frequently used by the chemist is potassium chlorate, which is composed of potassium, chlorine, and oxygen. At a comparatively low temperature the oxygen is driven off from the body, a compound of potassium and chlorine remaining behind—

$$2KClO_3 \quad = \quad 2KCL \quad + \quad 8O_2.$$
Potassium chlorate.   Potassium chloride.   Oxygen.

Experiment 30.—Using the same apparatus as that employed in the last experiment, substitute an ordinary test-tube,

placing in it about enough potassium chlorate to fill the bottom of the tube half an inch. As this liquefies on the application of heat, the tube must be inclined when fixed in the retort stand. Heat gently. At first the salt crackles; this is owing to the crystals being split up by the heat, and is known as *decrepitation*. The chlorate soon melts, and then appears to boil; the salt is really being decomposed. Collect the oxygen over the pneumatic trough and test it.

If, instead of using potassium chlorate alone, a mixture of that salt with about one quarter of its weight of manganese dioxide (black oxide of manganese) is employed, the gas is given off much more rapidly and at a lower temperature. At the end of the experiment the manganese dioxide is found unaltered. This mixture is almost always employed for the preparation of the gas, except when required in a condition of absolute purity.

The student will require seven jars of gas for the following experiments : it will be best to prepare them in two lots.

Experiment 31.—One-third fill a six-inch test-tube with the mixture of potassium chlorate and manganese dioxide in the proportions mentioned above : this amount is quite sufficient to
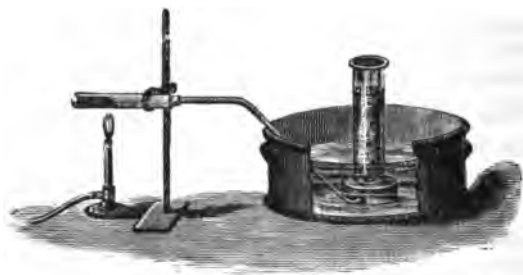
Fig. 14.—Collection of oxygen from potassium chlorate.

evolve the quantity of gas required. Push a wire down to the bottom of the tube, so as to make a clear passage for the gas. Connect the test-tube to the rest of the apparatus used in the last experiment, as shown in Fig. 14, and, having three jars

ready inverted in the trough, proceed to fill them. Holding the Bunsen in the hand, commence warming the mixture gently at the *top*, *i.e.* the end nearest the cork, and slowly bring the flame nearer the bottom as the gas is evolved. The reason for this is that the mixture cakes on being heated : if heated first at the bottom, the upward current of gas would carry the loose dust of the mixture on with it, and probably choke the leading tube. Withdraw the source of heat when the last jar is about half full : the action will then probably cease as the jar is filled. Remove the end of the leading tube from the trough ; otherwise, as the hot gas within cools, the contraction would draw up the water and crack the test-tube.

Experiment 32.—To one jar of the gas add some clear lime-water ; replace the plate, and shake up : observe that the lime-water remains clear. In the same jar make the usual test for oxygen.

Experiment 33.—To another jar add some litmus solution, and shake up : notice that the blue colour is unchanged.

Experiment 34.—In the third jar burn a piece of charcoal. Get a deflagrating spoon and cap ; see that it is clean by heating in the Bunsen. Push the spoon down through the cap, so that it will reach to about one-third the height of the jar from the bottom. Put the charcoal on the spoon and ignite with the Bunsen ; when glowing, plunge in the jar of oxygen ; it burns brightly. When the combustion is over, remove the deflagrating spoon, pour in some lime-water, and shake up ; the lime-water becomes milky.

For the remaining experiments two jars may be filled in the ordinary way ; another must be wiped perfectly dry and filled by downward displacement. For the next experiment obtain a deflagrating jar, *i.e.* one open at the top and bottom. Cork up the upper opening, and fill with gas; allow it to stand in the trough.

Experiment 35.—Take about four or five feet of fine iron binding wire ; make it into a spiral by winding round a test-tube, and weigh it carefully. Next fix it to the cap of a deflagrating spoon, and attach a small piece of vegetable tinder

(amadou) to the lower end; in the absence of this material, about a quarter of an inch of wax vesta may be used. The iron wire is now ready for burning. The deflagrating jar must be removed from the trough in a proper dish, in the bottom of which a piece of writing-paper has been placed, and allowed

to become saturated with water. There will thus be a layer of about half an inch of water at the bottom, then the paper, and underneath that another thin layer of water. Loosen the cork at the top, light the tinder or vesta, and immediately place the wire in the jar (Fig. 15). It burns brilliantly, throwing out a number of sparks, while from time to time drops of molten oxide fall to the bottom : these are so hot that if allowed to come in contact with the porcelain dish they would fuse into the glaze even after falling through an inch of cold water. The

FIG. 15.—Combustion of iron wire in oxygen.

writing-paper momentarily arrests them, and thus gives them time to cool. When the burning is over, remove the unburnt end of wire ; collect very carefully the whole of the globules of oxide of iron, place them in a crucible or evaporating-dish, and thoroughly dry them with a gentle heat. Weigh the oxide and the remainder of the iron ; there should be a sensible increase of weight over that of the iron alone previous to the burning ; the increase is, of course, due to the oxygen, which is also present in the oxide.

Another modification of this experiment demonstrates that iron increases in weight as a result of oxidation. Procure some clean iron filings, dry thoroughly at a temperature about that of boiling water, or by placing them in a thin layer in an oven. Weigh out 25 or 50 grams, and raise to a red heat in a platinum or clean iron dish. Stir them from time to time, so as to expose a fresh surface ; in about half an hour allow to cool and weigh. There is a considerable gain in weight resulting from the combination of the iron with oxygen from the air.

Experiment 36.—In one of the jars of gas, collected over the trough, burn a fragment of sulphur in the deflagrating

spoon; notice the brilliant light. Add to the jar after the burning some litmus solution; it is turned red.

Experiment 37.—In the other jar burn a piece of phosphorus the size of a small pea, remembering first to carefully dry it. The light produced is most brilliant. Add litmus solution, and observe that again the colour becomes red.

Experiment 38.—In the dry jar a piece of metallic sodium is to be burned. Sodium has such an affinity for oxygen that it requires to be kept in a liquid which does not contain that element: naphtha is usually employed. Cut off a little piece about the size of a pea, being most careful that the knife and everything which touches the metal is *perfectly dry*. Place in a clean and *dry* deflagrating spoon; heat in the Bunsen until it just glows, then put it in the jar of gas; it burns brightly: the products of combustion which are solid remain in the spoon. Allow it to get quite cold, then place the spoon in a little water in a beaker and dissolve off the oxide of sodium. To some litmus solution in a test-tube add just a drop of dilute sulphuric or nitric acid. Pour the red solution thus produced into the beaker containing oxide of sodium; the blue colour is restored.

Another method sometimes employed for the preparation of oxygen consists of heating to redness, in a closed iron tube, the black oxide of manganese. Unless large quantities of the gas are required, this method is now rarely employed; the gas is always impure from the presence of traces of chlorine, etc., from foreign substances contained in the oxide. The decomposition is thus represented:—

$$3MnO_2 = Mn_3O_4 + O_2.$$

Manganese   Trimanganic
dioxide.   tetroxide.
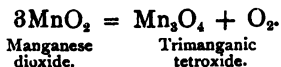
40. **Properties.**—Oxygen is a colourless, odourless, neutral, and non-inflammable gas, which until 1877 had never been liquefied. It is slightly soluble in water, one hundred volumes of water at 15° C. dissolving about three volumes of oxygen. Among its properties, by far the most important is that it possesses the power of supporting respiration. The gas in the pure state, however, is so active that a diluting agent is required; in the atmosphere this is

supplied by the presence of nitrogen in large quantity.   It also supports the combustion of inflammable bodies : substances which burn in air burn with increased brilliancy in this gas.   Its chemical activity is so great that, with the exception of fluorine, it combines with all the elements. The class of bodies thus formed is an important one, to which the name of *oxides* has been given.   The preceding experiments show the formation of several of these.   The composition of the bodies produced is shown in the following equations : —

$$C + O_2 = CO_2.$$
Carbon (charcoal).   Carbon dioxide.

$$3Fe + 2O_2 = Fe_3O_4.$$
Iron.   Triferric tetroxide.

$$S + O_2 = SO_2.$$
Sulphur.   Sulphur dioxide.

$$P_4 + 5O_2 = 2P_2O_5.$$
Phosphorus.   Phosphorus pentoxide.

$$4Na + O_2 = 2Na_2O.$$
Sodium.   Sodium oxide.
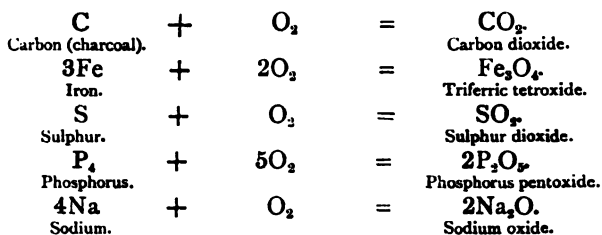
There is one important point of distinction between various oxides to which the student's attention will have been directed in the experiments already made : one group, of which sulphur dioxide is a representative, reddens a solution of litmus; another series, represented by sodium oxide, is characterized by the property of restoring the blue colour to litmus solution which has previously been reddened.   The oxides of the first group, when dissolved in water, produce *acids ;* those of the second group are known as *bases.*

41. Tests for Oxygen.—Oxygen is commonly recognized by its property of rekindling into a flame a glowing splinter of wood; but this property is also possessed by a gas called nitrous oxide, N_2O.   Their further distinction will be explained when describing nitrous oxide.

Ozone (Allotropic Oxygen). — Density, 23·94.

Specific gravity, 1·6584. Molecular formula and weight, O_3, 47·88.

42. Occurrence.—This gas, which has never been obtained in the pure state, is a curious modification of oxygen. Its density is exactly half as much again as that of oxygen. Traces of it are found in the air near the seaside and in the open country.

43. Preparation.—Ozone can be formed by the passage of a series of electric sparks through either air or pure oxygen, and may be recognized by its odour whenever an electric machine is worked. The quantity of oxygen thus changed is, however, very small, but if a *silent electric discharge* be passed through the gas, care being taken to avoid sparks, a much larger proportion of oxygen undergoes this transformation. In order to effect this, arrangements are made so that the discharge occurs between large surfaces placed very near each other.

Experiment 39.—For the performance of this experiment, special apparatus is necessary. This may be procured, or prepared in the following manner. A piece of thin, wide glass tubing, *a b*, as shown in A, Fig. 16, is closed at the bottom, except that a long piece of small-bore glass tubing, *c d e*, is sealed into it at *c;* this tube being bent over in the shape shown in the figure. Inside the tube *a b* is fixed another of smaller size, *f g*, open at the top, but closed at the bottom like a test-tube. These tubes are sealed to each other by fusion of the glass at *h;* immediately below this joint a side quill glass tube carrying a stop-cock, *i*, is fused into the outer tube. Between the tubes *a b* and *f g* there is consequently an annular space. If air be admitted at *i*, it traverses this space, and afterward makes its exit through the tube *c d e*. This constitutes the ozone producing apparatus proper : in B it is shown fixed in an outer jar, and provided with other fittings in order to provide means for passing an electric current from the surface of *a b* to that of *f g* across the intervening annular space, and through any

gas contained in that space. The ozone tube proper is simply drawn separately in A, in order that its construction may be more readily understood.
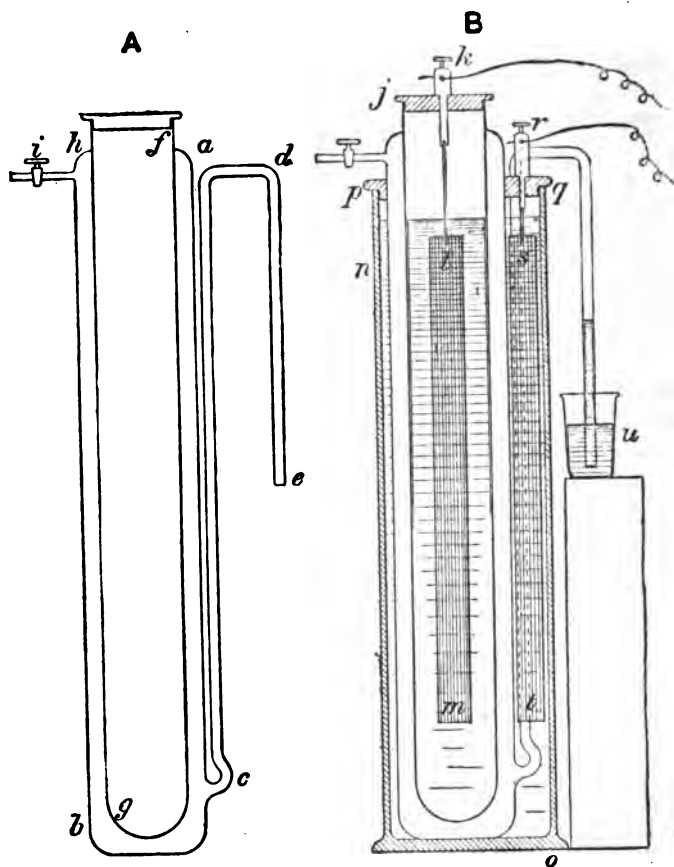
FIG. 16.—Apparatus for the preparation of ozone.

Turning to B, the tube fg is fitted with a cover, i, to which is attached a binding screw, k, and a platinum wire and sheet of

platinum foil, *l m* (electrode). The whole tube, *a b*, and inner limb, *c d*, of the small tube are contained within the outer glass jar *n o*, being held in their place by the cover *p q*. Through this cover passes a binding screw, *r*, carrying also a platinum electrode, *s t*. To use the apparatus, fill the outer jar *n o* nearly to the top with dilute sulphuric acid (1 to 10), and also fill the inner tube *f g* to the same level with the same liquid. To the binding screws *k*, *r* attach copper wires leading from the terminals of a powerful induction coil. On turning on the electric current, it is conducted, by means of the electrodes, to the dilute sulphuric acid, which again conducts it to the surfaces of the tubes *a b* and *f g* arranged within each other : it then passes across the ring-like space between as a silent discharge.

Having the apparatus in readiness, support a small beaker, *u*, containing water so as to receive the end *e* of the exit-tube. Open the stop-cock *i* and pass dry oxygen into the apparatus until it has displaced the air from the annular space between the tubes. (For this purpose, a volume of oxygen, some four or five times that of the annular space, should be passed through the tube.) Next close the stop-cock *i*, and observe that the tube *d e* is full of gas. Turn on the electric current from the induction coil through the apparatus ; ozone is gradually formed, and the water rises in the tube *d e*, showing that the volume of the gas within is diminishing.

Having noted the diminution of volume, remove the beaker *u*, and replace it by a small gas-jar arranged for collection by "downward displacement." Pass a slow current of oxygen through the stop-cock *i*, and collect the emergent gas in the gas-jar. Under the most favourable circumstances, however, the quantity of ozone produced by the transformation of oxygen does not amount to more than about one-sixth of the out-flowing gas.

Ozone may also be prepared by other methods, among which is that of the action of phosphorus on moist air.

44. Properties.—Ozone is a colourless gas having a density just 1·5 times that of oxygen. It has a faint, peculiar odour, sometimes described as resembling that of chlorine. Ozone is distinguished by its powerful oxidizing

properties.   Many of the metals, including even those so
difficultly oxidizable as copper, mercury, and silver, are
rapidly converted by ozone into oxides.   During oxidation
by ozone no diminution in the volume of the gas occurs.
The extra density shows that in ozone three volumes of
oxygen occupy the space of two volumes of the ordinary
gas ; hence the view that the ozone molecule contains three
atoms instead of two as in oxygen.   In oxidation by ozone,
it is the extra volume of oxygen which enters into combi-
nation, the normal oxygen set free occupying the same space
as the original ozone.   This is represented in the following
equation :—

$$\underset{\text{Ozone.}}{O_3} + \underset{\text{Silver.}}{2Ag} = \underset{\text{Silver oxide.}}{Ag_2O} + \underset{\text{Oxygen.}}{O_2}$$
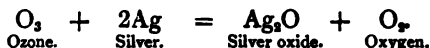
The oxidizing power of ozone leads it to immediately
decompose potassium iodide when the two are brought into
contact, oxidizing the potassium and liberating free iodine :—

$$\underset{\text{Ozone.}}{O_3} + \underset{\substack{\text{Potassium.}\\\text{iodide.}}}{2KI} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KHO} + \underset{\text{Iodine.}}{I_2} + \underset{\text{Oxygen.}}{O_2}$$
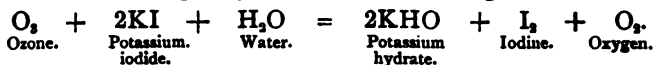
One characteristic of free iodine is that it forms a deep
blue-coloured compound on coming in contact with starch.
These properties of ozone and iodine respectively enable
us to test for ozone.

Experiment 40.—Put a piece of starch the size of a large
shot into a test-tube, and a quarter fill with water ; shake up and
then boil ; add a fragment of about the same size of potassium
iodide, and allow it to dissolve.   Dip some pieces of paper in
the solution, and introduce one into the jar of gas reserved from
experiment 39.   A blue tint is immediately produced on the
paper.   Notice also the peculiar odour of the gas.   Carefully
scrape a stick of phosphorus until quite clean, under water,
then place it in a gas-bottle and cover with a plate.   After the
phosphorus has been in the jar for about twenty minutes or
half an hour, introduce a piece of the starch and iodide test-
paper ; ozone, if present, will immediately produce a blue tint.
If the coloration does not at once appear, a piece of paper may
be left suspended in the jar, and will soon change colour.

Ozone is soluble in water, and imparts to it its characteristic odour. The colour of a solution of indigo is destroyed by the action of ozone, colourless compounds being formed which contain a higher proportion of oxygen.

Ozone very slowly decomposes into oxygen at ordinary temperatures. At a temperature of 237° C. the change is instantaneous, the gas, which contracted when the ozone was first formed, once more regaining its original volume. This change may be easily effected by passing the ozonized air or oxygen through a hot tube, when on its emergence all traces of ozone will have disappeared.

45. Allotropy.—Although oxygen and ozone present striking differences from each other, yet they are simply modifications of one and the same element. It has been explained that there is in this case a very simple difference in the constitution of the molecules, one containing two, and the other three atoms. Other elements also exist in two or more forms, due probably either to variations in the number of atoms in the molecule, or to variations in the method of their arrangement to form the molecule. **When an element occurs in two or more distinct forms it is said to exhibit allotropy, and the less common varieties are said to be allotropic forms of that element.** For this reason ozone is sometimes termed " allotropic oxygen."

Summary.

Oxygen is widely distributed. Discovered in 1774 by Priestley. May be prepared by decomposition of mercury oxide, chlorate of potash, and manganese dioxide. Manganese dioxide assists the decomposition of chlorate of potash without itself undergoing change. Forms compounds called oxides, one group of which reddens litmus ; another restores the blue colour. Properties : a colourless, odourless gas, non-inflammable, supporter of respiration and combustion, neutral to litmus solution.

Ozone is a condensed form of oxygen ; has a peculiar odour ; is produced in the passage of electricity through the air, also

during the oxidation of moist phosphorus ; is even more active as an oxidizing agent than oxygen ; is decomposed by a temperature of 237° C. into oxygen.

OBJECT DEMONSTRATION.

In Exp. 28, notice particularly the construction and principle of the apparatus. Observe also the red scales on the surface of the mercury and their likeness to the red oxide as prepared by other methods and supplied commercially.

Observe appearance and general characteristics of the following :—Potassium chlorate, a colourless salt occurring in flat or tabular crystals. Manganese dioxide, a heavy black powder, produced by grinding the mineral form of the substance ; compare with the appearance of the mineral in its natural state. Iron oxide, produced by combustion of iron in oxygen, consists of brittle molten globules. Sodium, a soft metal, very light, yet distinctly metallic in appearance and character.

Observe carefully the apparatus for the preparation of ozone.

Starch, a white powder, dissolves on heating to a pasty liquid. Potassium iodide, a white deliquescent salt occurring in cubical crystals.

LABORATORY DIRECTIONS.

In this chapter two very important experiments are described, the performance of which is generally confined to the lecture-table, viz. preparation of mercury oxide from the air, and preparation of ozone from oxygen. Note in each of these the general arrangement of the apparatus, and the principal lesson each experiment is intended to convey. Compare the directions given for collection of gas over mercury with those which follow for collection over water. Take the opportunity of studying the general manipulation of gas in a pneumatic trough with mercury.

The student will require the following pieces of apparatus before he proceeds with the preparation of the gases.

For generating apparatus No. 1, Fig. 14, take a test-tube three-quarters of an inch in diameter and 6 inches long. Select a cork which just fits it, after being rolled or squeezed in order to soften it. Take a piece of glass tubing 18 inches long, and

bend it to shape shown in figure. The best way to bend glass tubing is to hold it horizontally in a gas-flame (Fig. 17) from an ordinary burner, the long way of the flame. Keep twisting it round until it begins to soften, and then allow it to bend over to the right shape by its own weight. If this is done properly the tube
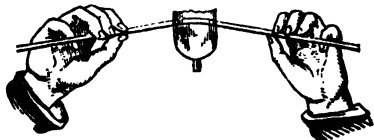
FIG. 17.—Bending glass tubing.

will assume a long uniform curve. Next, by means of the blow-pipe, make the ends of the tube just red-hot ; this will round off the sharp edges. Should it be necessary to cut the glass tubing to the proper length, this may be easily done by cutting a notch in the tubing with a triangular file, and then breaking by a kind of combined *pull* of the glass asunder and snapping it away from the notch. Next it will be necessary to bore a hole in the cork. For this purpose instruments called cork-borers are provided ; they consist of a set of thin brass tubes, the lower ends of which are sharpened. A rod is also contained in the set, in order to thrust out of the borers the pieces cut from the holes. The rod can also be pushed through two holes in the top of the borer, forming a handle to grasp when boring. Before commencing, see that the borer is clear ; then, beginning at the *small* end of the cork, bore carefully by twisting the borer and pushing it through. Take care, while going on, that the hole is *straight*. Do not place the cork against the bench and bore into the wood, as this blunts the borer. The hole should be *cut*, not bruised through. When finished, thrust out the boring with the rod. The borer selected should be one just a shade less in diameter than the glass tubing. Before pushing the glass tube into the cork, it may be advantageously touched over with a little grease. Hold the glass in a duster, so as to protect the hand in case it breaks. The cork and glass tube should fit perfectly air-tight ; lutings and cements of all kinds are unnecessary for the preparation of such apparatus, which the student should take the trouble to make properly in the first place, as so doing will save much time and vexation in after-experiments.

This completes apparatus No. 1, which is shown in use in Fig. 14. A couple of tubes should also be made of hard or

combustion tubing, which stands a much higher temperature than the other kind.   Take a piece of combustion tubing a foot long and warm it gradually in the middle over the flame of the foot-blowpipe, at first without blowing ; keep turning it in the flame ; when warm, increase the heat slowly by blowing, until at last the whole strength of the blowpipe is applied.   The glass will shortly soften, and then the two ends must be drawn asunder. Break off the connecting thread of glass close to the end of the tube ; fuse up the small hole with the blowpipe, and the tube is complete, with the exception of rounding the edges of the open end in the flame, which must be done when the bottom is cool. Such tubes must be allowed to cool slowly, or else there is danger of their cracking ; for the same reason, they must be heated very carefully and gradually when in use.

No. 2 apparatus should now be made.   Fit a good cork to the 16-oz. flask ; take 6 inches of glass tubing and bend it in the middle at right angles, always remembering to round off the ends.   Bore two holes through the cork, one to fit this and one the thistle funnel.   The glass bend should be just pushed through the cork, and the funnel should reach to within a quarter of an inch of the bottom of the flask.

No. 3 apparatus consists of an 8-oz. flask, to which a cork is fitted with two holes ; through one is passed a bent tube reaching the bottom of the flask, and through the other a short bend like that in No. 2 apparatus.   This same flask should also be provided with a cork with one hole and a single glass bend (No. 4).   The three are shown in Fig. 18.
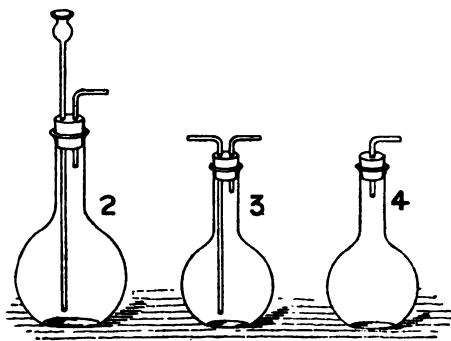
FIG. 18.—Gas apparatus.

The whole of these should be constructed at the outset; they will be found sufficient for the preparation of most of the .gases. If thoroughly cleaned immediately after use, they should last through the whole course of experiments.

In the special sketches subsequently given the student may often adapt bent glass tubes already made by the use of india-rubber connections, instead of making new ones of the exact shape shown.

The terms "leading tube" and "delivery tube" are applied to the tube by which a gas emerges from any particular piece of apparatus.

For the collection of gases by displacement and other pur-poses, a piece of glass tubing about 14 inches in length should be bent at right angles 3 inches from one end.

For experiments gases are usually collected in gas-jars or bottles. For ordinary purposes of the student, wide-mouthed bottles do very well about the size of a common pickle-bottle ; they should, however, be of white glass. The gas is best retained in the bottle by placing a ground glass plate on the mouth, which must be ground flat. This is very easily and quickly performed in the following manner : Procure a piece of plate-glass about 6 or 8 inches square ; place on it some emery of medium coarseness and water. Take the bottle, hold it firmly mouth downward on the plate, and rub with a circular motion. Half a minute's rubbing will generally suffice to grind the top true. The joint between the glass plate and the bottle is rendered air-tight by smearing the plate with a little grease. The resin cerate of the druggist answers this purpose admirably.

Gases which are insoluble or only slightly soluble in water are best collected over the pneumatic trough. One of the most convenient forms of this apparatus is a circular basin of earthen-ware, and a little stand known as a beehive shelf on which the inverted jar is placed. To use the trough, proceed in the follow-ing manner : Put sufficient water in the trough to cover the beehive shelf ; then, having ready the jars and plates, fill each jar with water, put on the plate, turn it upside down, and place the mouth of the jar under the water in the trough : on with-drawing the plate the jar remains filled from the pressure of the atmosphere. If there is room, all the jars should in this way be placed in the trough. Next place the leading tube from the generating apparatus under the shelf, and when the gas has

driven the air out of the apparatus, begin to collect by placing one of the bottles on the shelf.   Have ready its plate ; when it is full remove it and substitute another, taking care to keep• their mouths under the surface of the water during the whole operation.   Next close the mouth of a full bottle with a plate, and take it out of the trough.   Fig. 14 shows a jar placed for the collection of gas, the front of the trough being removed in order to show the beehive shelf.

Gases which are soluble in water must be collected another way.   They are sometimes collected in a pneumatic trough over mercury.   In general, however, the process of displacement is used.   In this operation the gas is poured into the bottle and drives the air out.   In cases where the gas is heavier than air, stand the bottles upright, and let the leading tube from the generating apparatus reach to the bottom of the bottle. Cover the top with a piece of cardboard, in order to prevent the escape of gas by diffusion.   In order to find out if the bottle is full, test from time to time near the mouth.   The test employed must depend on the nature of the gas ; oxygen may be recognized by its power of igniting a glowing splinter.   When full, close with a plate.

When the gas is lighter than the air, the whole arrangement must be inverted : the gas is then said to be collected by upward displacement.

CHAPTER V.

HYDROGEN.

Symbol, H. Atomic weight, 1. Density, 1. Specific gravity, 0·0691. Molecular formula and weight, H_2, 2. Boiling-point, $-140°$ C., under 650 atmospheres.

46. Occurrence.—Hydrogen occurs in the free state in the gases evolved from certain volcanoes, and at times among the products of putrefaction. Spectrum analysis also reveals free hydrogen as a constituent of certain stars and nebulæ. Hydrogen is chiefly found in combination with oxygen in water, which compound consists of one part of hydrogen united with eight parts of oxygen by weight. This gas was discovered by Paracelsus in the sixteenth century, and was systematically investigated by Cavendish, who, in 1781, demonstrated the elementary nature of this gas.

47. Preparation.—The attraction of the metals sodium and potassium for oxygen is so great that they readily decompose water, setting free the hydrogen, which, with sufficient care, can be collected.

Experiment 41.—Drop a very small piece of sodium into a trough of water; notice that it melts, and, rushing round on the surface for some time, becomes smaller and finally disappears.

Next, place a piece of either filter or blotting paper on the surface of the water, and drop a fragment of sodium on the paper; it soon melts, and then takes fire, burning with an intensely yellow flame.

Drop a piece of potassium in water; it at once takes fire, and burns with a flame of a characteristic violet colour. In this case the intervention of filter paper is unnecessary.

The combination of sodium and potassium with oxygen, even under these circumstances, is accompanied by considerable heat, which inflames the hydrogen gas displaced from the water by the action of the metal. It is this gas which produces the flame : the characteristic tint in each case is due to the presence of the vapour of each metal.

In any of these experiments with sodium or potassium and water in which the escaping gas should take fire, stand some little distance until it has burnt out, and then wait until the molten hydrate, which at first floats on the surface of the water, is dissolved ; at this moment there is always a slight spit, and there is the danger, if a person is standing immediately over it, that portions of the hydrate may get into the eye. It would be wiser for the student to omit these experiments until he has first seen them performed by the teacher.

If the globule of metal, instead of being allowed to float on the water, is held under the surface, bubbles of gas are seen to arise ; these consist of hydrogen, and may be collected in the following manner : First fold a piece of fine wire gauze into a cone in precisely the same manner as directed in Exp. 19 for the preparation of a filter paper. Have in readiness a pair of tongs, by which this may be held point upwards under the water. Place in the trough a small stout glass jar, inverted and full of water, ready for collecting the gas ; be sure that not a bubble of air remains in it. Throw a piece of sodium about the size of a pea in the water, and at once depress it beneath the surface with the gauze cone, held in the tongs like a candle extinguisher. Wait until after the first bubble of gas has arisen ; then hold the jar over the rising gas, and thus collect it. Repeat this operation with fresh pieces of sodium, until the jar is filled. Apply a light to the jar of gas ; it burns with a pale flame tinged yellow by the sodium vapour.

The chemical change is thus represented :—

$$2\text{Na} \quad + \quad 2\text{H}_2\text{O} \quad = 2\text{NaHO} \quad + \quad \text{H}_2.$$

Sodium.   Water.   Sodium hydrate,   Hydrogen.
                        or hydroxide.
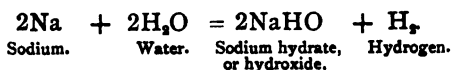
Experiment 42.—Take another fragment of sodium and dissolve in a small quantity of water in an evaporating basin; when the action is over, observe the soapy feel which the liquid gives to the fingers: this is a characteristic of the class of bodies of which sodium hydrate is a member. Evaporate to dryness, and notice that a white solid substance remains.

Sodium hydrate is frequently called caustic soda, or soda only, for the sake of brevity. The formula of sodium hydrate shows that it contains hydrogen; in fact, it may be regarded as water in which one of the atoms of hydrogen has been replaced by sodium. It is possible to also displace the second atom of hydrogen by sodium, thus forming sodium oxide, Na_2O, according to the equation—

$$2NaHO \quad + \quad 2Na \quad = \quad 2Na_2O \quad + \quad H_2.$$
Sodium hydrate.   Sodium.   Sodium oxide.   Hydrogen.
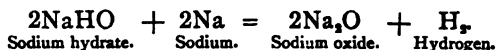
This second atom of hydrogen may also be displaced by either zinc or aluminium, which elements have the advantage of being more easily manipulated than sodium.

Experiment 43.—Fit a 4-oz. flask with cork and single delivery tube; put in a small quantity of zinc and a piece of solid sodium hydrate about the size of a hazel-nut; add just sufficient water to cover the bottom of the flask. Fix in the retort stand and apply heat. At first bubbles of air come over, but when the sodium hydrate is melted, hydrogen is evolved, and may be collected over the pneumatic trough. The water takes no part in the chemical action, but is simply added to prevent the heat from cracking the flask.

The following is the reaction which occurs:—

$$2NaHO \quad + \quad Zn \quad = \quad ZnNa_2O_2 \quad + \quad H_2.$$
Sodium hydrate.   Zinc.   Sodium zinc oxide.   Hydrogen.
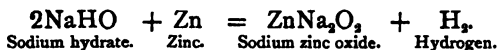
The most interesting point about these two experiments is, that by means of them we succeed in obtaining hydrogen from water in two distinct instalments; proving that at least two atoms of hydrogen are present in the molecule of water. Making use of an atomic instead of a molecular

equation, the two successive displacements of hydrogen may be thus represented :—

$$HHO \quad + \quad Na \quad = \quad NaHO \quad + \quad H.$$
Water.   Sodium.   Sodium hydrate.   Hydrogen.

$$NaHO \quad + \quad Na \quad = \quad NaNaO \quad + \quad H.$$
Sodium hydrate.   Sodium.   Sodium oxide.   Hydrogen.

$$NaNaO$$
Sodium oxide.
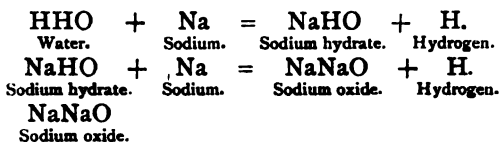
Written in this manner, the replacement of the hydrogen by sodium in two steps is shown very clearly.

There are several other metals beside sodium which are able to decompose water; some of them, however, require a higher temperature. Iron is one of these metals. The decomposition is most readily effected in the following manner :—

Experiment 44.—Take an iron tube about an inch in diameter ; fill it with loose iron turnings, and heat to redness in
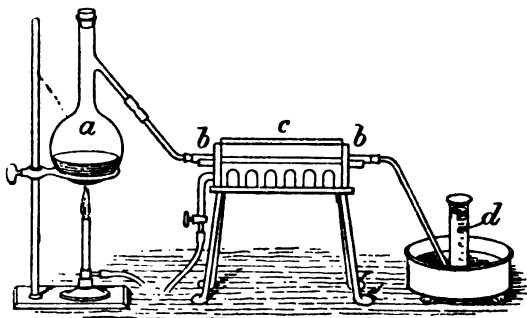
FIG. 19.—Decomposition of steam by red-hot iron.

a Fletcher's gas-tube furnace, *c*, as shown in Fig. 19. Arrange a side-tube flask, *a*, for the generation of steam, and attach it by means of glass and indiarubber tubes and corks to the iron tube *b*. The steam which enters *b* is decomposed ; hydrogen escapes, and is collected in the jar *d*.

The change is thus represented :—

$$3Fe \quad + \quad 4H_2O \quad = \quad Fe_3O_4 \quad + \quad 4H_2.$$
Iron.   Water.   Triferric tetroxide.   Hydrogen.

The oxide of iron, Fe_3O_4, produced in this experiment is magnetic, and, unlike the oxide developed on iron by exposure to the atmosphere (Fe_2O_3), is *adherent*, and a protective from further rust. Barff's process for preventing articles from rusting is an application of this principle.

While certain metals are thus able to decompose water with the evolution of hydrogen, there are others, of which copper is an instance, that are unable to decompose water at any temperature.

The most convenient method for preparing hydrogen consists of acting on either commercial zinc or iron with dilute hydrochloric or sulphuric acid. As a rule, zinc and sulphuric acid are employed. The gas comes off readily and at the ordinary temperature :—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
Zinc.   Sulphuric acid.   Zinc sulphate.   Hydrogen.
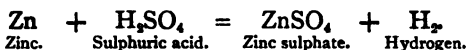
Experiment 45.—Place about half an ounce of granulated zinc in the flask of No. 2 apparatus ; to the delivery tube attach the bent glass tube of the apparatus No. 1 by means of a piece of indiarubber tubing, and arrange for the collection of the gas with the pneumatic trough. Pour about 4 ozs. of water in the flask through the thistle funnel. Next add a very little concentrated commercial sulphuric acid ; about a teaspoonful is sufficient. Give the flask a shake ; immediately there is a brisk effervescence, and the gas may be readily collected over the trough. More sulphuric acid should be added as the action slackens. Apply a light to the first jar that comes over ; it detonates somewhat violently, from the fact that it contains a mixture of hydrogen and air, which is explosive. The second may very possibly also contain air ; the third jar will probably be filled with pure hydrogen. Collect now four jars for experiment.

Although hydrogen is thus readily evolved from sulphuric acid by the action of ordinary zinc, the pure metal is without action on the dilute acid. Commercial zinc contains traces of other metals : these set up a voltaic (electric) action when placed in action, and so cause its decomposition with evolution of hydrogen. This effect of the

impurities of ordinary zinc may be avoided by first coating
the zinc with mercury. This is done by first thoroughly
cleaning the metal with sulphuric acid, and then rubbing
mercury over the surface until thoroughly bright. This
operation is termed amalgamation. That the effect is due
to the presence of impurity is shown by adding a small
quantity of a solution of either a lead or copper salt to pure
zinc and dilute sulphuric acid, when hydrogen gas is at once
evolved.

Experiment 46.—Add some dilute sulphuric acid to a little
pure zinc ; notice that no gas is evolved. Amalgamate a strip
of ordinary zinc, and also observe its action when placed in
dilute sulphuric acid. To the amalgamated zinc and acid add
two or three drops of copper sulphate solution ; gas is at once
evolved.

The copper sulphate thus added is first decomposed
according to the equation following; the liberated copper
then forms a voltaic couple with the zinc :—

$$\underset{\text{Copper sulphate.}}{CuSO_4} \; + \; \underset{\text{Zinc.}}{Zn} \; = \; \underset{\text{Zinc sulphate.}}{ZnSO_4} \; + \; \underset{\text{Copper.}}{Cu.}$$
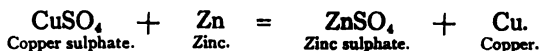
48. Properties.—*Experiment* 42.—Hold a jar of gas
mouth downward ; apply a light : the gas burns at the mouth
with a non-luminous and almost colourless flame. Thrust the
taper up into the jar ; the taper is extinguished, but the gas
continues to burn.

The combustion of hydrogen in oxygen or atmospheric
air produces water :—

$$\underset{\text{Hydrogen.}}{2H_2} \; + \; \underset{\text{Oxygen.}}{O_2} \; = \; \underset{\text{Water.}}{2H_2O.}$$

All gases evolved from mixtures in which water is
present contain aqueous vapour; therefore, before attempt-
ing to prove the presence of water as a result of the
combustion of hydrogen, we should first *dry* the hydrogen
itself. This is easily effected by passing the gas over some
substance which has an attraction for water : the most

important desiccating or drying agents used by the chemist are calcium chloride, sulphuric acid, and quicklime. Whichever of these is selected must depend on the nature and properties of the gas to be dried. Hydrogen may be dried by the use of either calcium chloride or sulphuric acid.

Experiment 47.—Select a piece of glass tubing of half an inch or five-eighths bore and about 9 inches long, round off the ends with the blowpipe and fit a cork to each. To the one cork fit a tube bent at right angles, with the end drawn out to a jet ; through the other pass a piece of tubing bent to the shape shown in Fig. 20 ; or simply fit it to a straight piece of glass tube, and connect to the leading tube of the generating flask with indiarubber tubing ; this part of the apparatus would then have to be supported by the retort stand. Fill the large tube with small fragments of calcium chloride, and place at each end, between the chloride and the cork, a plug of cotton-wool. A slow current of gas passed through this apparatus will emerge in the dry state. If necessary, place some more zinc and sulphuric acid in the generating-flask ; let the gas escape until a jar collected burns quietly without explosion ; then attach the drying-tube, and after a few seconds light the gas as it issues from the jet.

FIG. 20.—Production of water by the combustion of hydrogen.

Too much stress cannot be laid on this injunction, to FIRST *see,* BEFORE *lighting the jet, that a collected jar of the gas burns quietly. Want of attention to this direction will lead to* EXPLOSION *of the whole apparatus.* Take a glass tube 18 inches or 2 feet long, and about half an inch diameter ; if necessary, dry the inside by pushing a plug of cotton-wool through ; hold it over the jet : the watery vapour condenses in the cooler parts of the tube.

This experiment is often accompanied by a peculiar

musical note produced by a rapid series of small explosions within the long tube. The moisture which condenses on a kettle or other vessel of cold water heated over a gas stove, is the product of combustion of the hydrogen of the coal gas.

Hydrogen is the lightest substance known, and for this reason is conveniently chosen as the standard for comparison of other gases: its buoyancy has led it to be used for the purpose of filling balloons; coal gas, from its greater cheapness, is, however, usually preferred. The following experiments are illustrative of this property :—

Experiment 48.—Take a jar of the gas, and, setting it down mouth upwards, take off the glass cover ; after the expiration of thirty seconds apply a light ; the gas will be found to have entirely escaped. Take a second jar, and, holding it mouth downwards, remove the glass plate ; let it also remain for thirty seconds, and apply a light ; the gas will take fire and burn as usual, but little of it having escaped.

From its great lightness, this gas may be poured upward from jar to jar. Take an empty jar, invert it, and, removing the plate from a full one, pour the gas *up* into it. In ten seconds place a light to each jar ; the gas in the inverted one will burn, the other will be found to contain no hydrogen.

49. Gaseous Diffusion.—One distinguishing property of gases is the readiness with which they mix with each other. This is noticed especially with those gases possessing a characteristic odour: thus, if a gasburner be left open for even two or three minutes, the smell of coal gas may be detected over every part of a large room. **The natural process by which one gas is thus disseminated through another is termed "gaseous diffusion."** It takes place between all gases, even though the heavier is first at the lower level. In other words, a heavy gas will diffuse up into a superincumbent light gas, while the light gas will make its way downwards and mix with the heavier one. In this way different gases, when placed in the same space,

rapidly produce of themselves a uniform mixture. This process of diffusion will also go on through a porous membrane, as, for example, a thin diaphragm of plaster of Paris or porous earthenware. Thus, if a vessel be divided into two parts by a thin partition of porous material, and the one half be filled with one gas and the other with another, they will be found after some time to have become thoroughly intermixed with each other. The rate of diffusion of all gases through such a diaphragm is not the same, but depends on their densities. **The rate of diffusion of gases is inversely as the square root of their density.** Thus, hydrogen and oxygen have respectively densities of 1 and 16; hydrogen diffuses four times as rapidly as does oxygen. The rapid diffusibility of hydrogen is illustrated in a striking manner by the following experiment :—

Experiment 49.—Take a piece of glass tubing some ten or twelve inches in length, and proceed to close the one end with a layer of plaster of Paris in the following manner. First mix a little of the plaster with water, so as to form a thick cream ; spread this mixture uniformly on a plate to the depth of an eighth or three-sixteenths of an inch. Then press down in it one end of the clean dry glass tube, and allow it to remain undisturbed until the plaster has "set" (become solid), which should take place in ten or fifteen minutes. Slide the end of the tube off the plate, and place it on one side for a day to dry.

Cover the plaster diaphragm with a cap of tinfoil and fill the tube with dry hydrogen by upward displacement. Place the inverted tube with its lower end in the water of a pneumatic trough, and about half an inch below the level of the surface. For this purpose put a beehive shelf in the trough and fill with water, until the level is a half-inch above the top of the beehive. Remove the tinfoil cap and immediately the water is seen to rise within the tube against the action of gravity until the tube is about two-thirds full of water. As a converse experiment, the tube may be filled with carbon dioxide, when the level of the gas descends and displaces the water altogether from the tube.

In this experiment the hydrogen, being so much lighter

than air, diffuses out through the diaphragm nearly four times as rapidly as the air diffuses in; the consequence is that the volume of gas in the tube rapidly lessens and the water rises.

50. Reducing and Oxidizing Agents.—The ores or natural compounds from which metals are derived are in many cases oxides or sulphides of such metals. The operation of obtaining the metal in its free state is termed *reducing* the ore to its metallic state. Hence we get the definition that **a reducing agent is a substance which removes oxygen, or elements similar to it, from compounds.** Owing to the avidity with which hydrogen combines with oxygen, it constitutes one of the most powerful reducing agents with which we are acquainted. Thus, if hydrogen be passed over red-hot copper oxide, or iron oxide, the metal is obtained in the free state, according to the following equations :—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O.}$$
$$\underset{\text{Iron oxide.}}{Fe_2O_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Iron.}}{2Fe} + \underset{\text{Water.}}{3H_2O.}$$
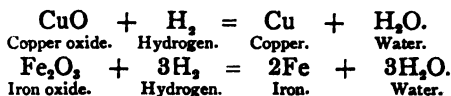
It may be pointed out, in passing, that hydrogen, a gas that may be produced by the reducing action of iron on steam, is here passed over copper oxide, a product of the oxidizing influence of the oxygen of the air on copper.

Experiment 50.—Take a piece of combustion tubing, about 14 or 16 inches in length, and fit a cork and piece of small glass tubing to the one end. Introduce some powdered oxide of copper into the tube, and about 4 inches from the corked end. Fix the tube horizontally in a retort-stand, and pass dried hydrogen through it. As soon as the whole of the air is expelled, apply heat by means of a Bunsen to the part of the tube containing the copper oxide. Notice after a time that water in considerable quantity condenses in the cooler part of the tube, and that the black oxide changes in colour to the characteristic red tint of copper.

The reaction of hydrogen with copper oxide is of considerable importance, as, in the analysis of many compounds containing hydrogen, the hydrogen is thus converted into water and weighed as such. In addition to these instances, in which a reducing agent is employed in order to obtain metals in their free state, there are other examples of reduction in which the bodies are simply reduced to a lower stage of oxidation. Further, the same reducing agents are capable of removing, in whole or in part, chlorine and other similar elements from compounds. Among the most active reducing agents, in addition to hydrogen, are carbon, carbon monoxide, zinc, sodium carbonate, and sulphurous acid.

We come next to a class of bodies which are just the exact opposite of the reducing agents; these are termed oxidizing agents, and are described in the following definition : **An oxidizing agent is a substance which causes an element or compound to combine with oxygen or other elements of similar character.** Oxygen, and especially ozone, are the most familiar and direct examples of oxidizing agents. If metallic copper be heated in a current of oxygen, the following reaction occurs :—

$$2Cu + O_2 = 2CuO.$$
Copper.   Oxygen.   Copper oxide.
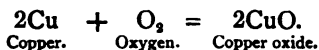
The following are some of the most important oxidizing agents : oxygen, ozone, chlorine, bromine, potassium chlorate, nitric acid, and hydrogen peroxide.

51. Nascent Condition of Elements. — It has already been explained that the atoms of elements unite to form what are termed elementary molecules. It will be readily understood that some portion of the energy which impels atoms to unite with other atoms is thus consumed; in consequence it is found that elements in the atomic state are more active than those same elements when in the molecular condition.

Experiment 51.—Take some solution of ferric chloride,

notice that it has a sherry red tint. Bubble hydrogen gas through the solution ; notice that no alteration in colour occurs. Next add to the solution a little sulphuric acid, and then drop in a few fragments of zinc ; the colour very quickly disappears.

In this second case the hydrogen is generated within the solution, and the liberated atoms at once act on the ferric chloride. In the first case the hydrogen has formed molecules, and has not sufficient energy to effect the reduction of the chloride. The following equation shows the chemical changes which occur :—

$$Zn + H_2SO_4 = ZnSO_4 + 2H.$$
Zinc.   Sulphuric acid.   Zinc sulphate.   Nascent hydrogen.

$$2H + Fe_2Cl_6 = 2FeCl_2 + 2HCl.$$
Nascent hydrogen.   Ferric chloride.   Ferrous chloride.   Hydrochloric acid.
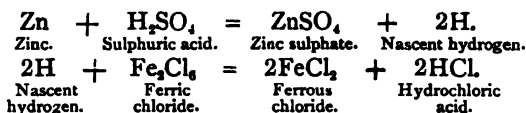
An essential of this type of chemical action is that it is caused by an element at the moment of its being liberated from a chemical compound. Therefore, **at the moment of liberation from a compound an element is said to be nascent, a word signifying being born.** Many elements possess more active chemical properties when in the nascent state, the reasons for which should now be clear to the student. When elements are in the molecular state, the force by which the atoms are held together must be overcome before they can enter into fresh combinations. When they are in the nascent condition no such force has to be overcome, and so the atoms are able to enter into combinations much more readily.

52. Properties of Hydrogen (*continued*).—The foregoing experiments show that this gas is colourless, odourless, tasteless, inflammable, and a non-supporter of combustion. It is of very low density, and consequently diffuses itself through other gases with great rapidity. Hydrogen is a powerful reducing agent, especially when in the nascent condition.

The gas prepared from zinc and sulphuric acid has

generally a slight odour from the presence of impurities in the zinc and acid; when the gas is required in a state of absolute purity, this is ensured by the use of pure reagents. Should iron be used instead of zinc for its production, the smell is much stronger, through the presence of compounds of hydrogen with carbon, carbon being an invariable constituent of common iron. The gas is not poisonous, but animals placed in it soon die from simple deprivation of oxygen. It is very slightly soluble in water, 100 volumes dissolving only 1·93 volumes of the gas. In many of its chemical relationships hydrogen behaves rather as a metal than a non-metal.

It will be remembered by the student that hydrogen, in common with oxygen, is one of the gases which have been liquefied by MM. Cailletet and Pictet.

Summary.

Hydrogen is principally found in water. May be prepared by the action of metals on that liquid, as sodium, iron, etc. ; also by action of zinc or iron on various acids.

Hydrogen is a colourless, odourless, and tasteless gas, inflammable, a non-supporter of combustion. It is also neutral to litmus solution, it is the lightest body known, and is a powerful reducing agent.

OBJECT DEMONSTRATION.

Observe the general appearance of both potassium and sodium, especially that, although coated with a thin film of tarnish, they are bright and metallic when cut.

Note the construction and use of the gas-tube furnace.

Observe the gas-diffusion apparatus, and especially the porous plug of plaster of Paris.

LABORATORY DIRECTIONS.

The experiment on decomposition of water by red-hot iron is one usually confined to the lecture-table : study the apparatus carefully, and note the important fact of hydrogen being evolved.

The gas-diffusion experiment is also one not generally performed by the individual student, therefore examine very carefully the apparatus, and the mode of using same. The other experiments call for no very special remark.

It must not be forgotten, in dealing with sodium, that the fingers must be perfectly dry.

In collecting hydrogen from sodium hydrate and zinc, if the neck of the flask has been touched with the soda, there is frequently difficulty in keeping the cork in from its consequent soapiness. This may generally be prevented by just touching round the cork with dilute sulphuric acid.

Great care must be taken in mixing sulphuric acid and water ; if the directions given are followed there need be no fear. On no account add the water to the sulphuric acid.

Never omit the precautionary measures given before lighting a jet of hydrogen.

In handling chloride of calcium, place it in the drying tube as quickly as possible, and *immediately* replace the cork in the jar containing it.

CHAPTER VI.

OXIDES OF HYDROGEN.

Two oxides of hydrogen are known : —

Hydrogen monoxide, or water, H_2O.
Hydrogen peroxide, or hydroxyl, H_2O_2.

Water.—Formula, H_2O. Molecular weight, 17·96. Density, 8·98. Specific gravity as steam, 0·622. Specific gravity as liquid, 1·00. Melting-point, 0° C. Boiling-point, 100° C.

Water is taken as the standard of specific gravity of liquids and solids.

53. Occurrence.—Water is found in nature in the three distinct forms of ice, water, and steam. Its appearance and ordinary physical characters are so well known that any description is unnecessary.

54. Preparation.—Water naturally occurs so plentifully in an almost pure condition, that, except when required for chemical purposes, no special processes of preparation are needed. Chemically pure water is usually obtained by freeing natural water from the small quantity of foreign substances which it contains. As most of these are solid bodies in a state of solution, the water is commonly purified by the process of distillation, an operation already described on p. 42.

55. Properties.—Between the temperatures of o° and 100° C. water is a tasteless liquid, and without colour, except when seen in large masses. A layer of pure water some 12 feet in length shows a faint greenish-blue tint. The most important property of water is its great solvent power, there being comparatively few substances which it does not dissolve in more or less quantity. In consequence, water is never found in a state of absolute purity in nature. The sea is the natural reservoir from which our water-supplies are drawn. By the sun's heat, enormous quantities of sea-water are converted into vapour, which remains in the air in the gaseous form, or condenses to produce clouds. Special atmospheric conditions lead to the precipitation of this moisture as snow or rain. This form of water is about the purest of those occurring naturally; but even rain-water is contaminated with gaseous impurities absorbed from the atmosphere, and also small quantities of solid matter which have been floating in the air in a minute state of subdivision. Rain and snow are the direct or indirect sources of spring and river waters; these latter always contain more or less solid matter, depending on the nature of the rocks and soil of each particular district. The rivers carry down with them solid matter to the ocean, which solid matter remains when the water is again evaporated to form clouds. There is thus a continuous, though slow, increase in the quantity of matter found in sea-water, which, as a result, has its well-known saline flavour. The constitution of sea-water varies in different parts, but its principal solid constituent is common salt, or sodium chloride, NaCl. The sea contains in addition smaller quantities of magnesium and other salts, of which the compounds of bromine and iodine are of most importance.

Experiment 52.—Evaporate to dryness on a clean piece of platinum foil a few drops of common water; notice that a perceptible residue remains; contrast with that obtained from distilled water.

Experiment 53.—Take an 8-oz. flask fitted with cork and single bent tube, as shown in Fig. 18 ; attach with india-rubber a glass tube, leading into the pneumatic trough ; fill the flask to overflowing with cold spring or rain water ; push in the cork ; the water displaced will drivè the air from out the leading tube. Heat the water with the Bunsen, and place a large test-tube to collect in the ordinary manner the gas which is evolved ; let the water boil until no more gas is disengaged.

In this way an estimate may be made of the quantity of air, and other gases, the water, when cold, held in solution. This quantity, though small, is of great importance, being the supply from which fishes derive the oxygen necessary for the support of respiration, and aquatic plants the carbon dioxide requisite for their growth and development. The experiment also shows that gaseous impurities are not separated from water by distillation, being carried over by the steam.

Water is distinguished from all other liquids by its freedom from colour (in small quantities), taste, and smell. Further, it is neither acid nor alkaline in its properties, and evaporates completely away on being heated, leaving no residue. In addition, it is neither inflammable nor a supporter of combustion.

56. Effects of Heat on Water.—Among the proper-ties of water, the physical changes it undergoes as a result of the application of heat are of such importance as to warrant a somewhat extended description. As is well known, at a temperature below the freezing-point water exists in the solid state and is known as ice. Taking a piece of ice at a temperature much below that at which it was formed, say —20° C., the following is a history of its changes as a result of the continuous application of heat. As heat is first applied, the ice rises in temperature and at the same time increases in volume (expands) ; these changes proceed regularly until a temperature of 0° C. is attained. At that point the temperature remains stationary,

notwithstanding that the absorption of heat continues.
During this time the ice melts, and the heat thus absorbed,
without causing any corresponding elevation of temperature,
is employed in doing the work of converting the solid ice into
liquid water.   The heat necessary to melt a given weight of
ice at 0° C. into water at the same temperature would raise
the same weight of water from 0° to 79° C. ; a fact which is
expressed in other words by saying that the latent heat of
water is 79 heat-units.   During the melting of ice a con-
siderable diminution in volume occurs, 10 volumes only of
water being produced from 10·9 volumes of ice.   As soon
as the whole of the ice is melted, the temperature once
more commences to rise, and does so steadily until a
temperature of 100° C. is attained.   The water at 0° C.
diminishes in volume with an increase in temperature, until
at 4° C., when it commences to expand, and continues to
do so until 100° C. is reached.   At 4° C., therefore, water
is at its maximum density ; either an increase or diminution
of temperature results in expansion.   At 100° C. the water
commences to boil and remains stationary in temperature,
but is not all at once converted into vapour ; on the con-
trary, between five and six times as long is necessary to boil
away the whole of the water as was requisite in order to
raise it from the freezing to the boiling point.   In exact
figures, the quantity of heat necessary to convert a given
weight of water into steam is sufficient to raise 537·2 times
the weight of water from 0° to 1° C.   The steam produced
is at the same temperature, 100° C., as the boiling water ;
this large amount of heat is employed in the conversion of
the water from the liquid to the gaseous state.   The whole
of the water having been converted into steam, a further
application of heat results in the expansion of the steam,
which follows the general laws governing the relation of
gases to heat.

In cooling, steam passes through a series of changes
which are just the converse to those it experiences on being

heated. During the condensation of steam into water, and the solidification of water to form ice, heat is liberated in the same quantity as was required in the first place to effect respectively the liquefaction of ice and the conversion of water into steam.

57. Tension of Aqueous Vapour.—Water gives off, at all temperatures, vapour, which exerts a definite pressure; as the temperature rises the pressure of the vapour also increases. At the boiling-point of water, or any liquid, the pressure or tension of its vapour is equal to that of the atmosphere. This fact may be easily proved by experiment.

Experiment 54.—Take a U tube A, as shown in Fig. 21, with one end sealed; the limbs of the tube may be from about 1 foot to 18 inches long and three-eighths of an inch diameter. Pour in a few drops of water, and let them run round to the sealed end; next fill with mercury, so that the metal shall stand at the bottom of the straight portion of the open limb of the tube, the closed one being full; the mercury is retained in position when the tube is upright by the pressure of the atmosphere; on its surface in the sealed end a few drops of water will be seen floating. The sealed limb must now be enclosed in a jacket (B) composed of a glass tube sufficiently wide (about 1 inch diameter) to permit of the passage of steam between the two glass tubes. Fit the steam jacket with two corks; fix a glass bend to the upper one; and through the lower bore one hole in the centre for the U tube, and another in which must be introduced a glass tube to lead away the waste steam. Fix the apparatus upright in the retort-stand, and pass steam through the jacket from water boiled in a flask; as the temperature of the jacket rises, the mercury is depressed, until it at last is stationary, and at a level in the two limbs of the U tube.

The mercury in the outer limb is subjected to the pressure of the atmosphere, that in the inner to the pressure of the steam; the surfaces being level with each other is a proof that the two pressures balance, and therefore the

boiling-point of a liquid is that at which the tension of its vapour equals that of the atmosphere.

It follows that if the pressure on a liquid be varied, its boiling-point also changes; if a few drops of water be placed in the vacuum at the top of the mercurial column of the barometer, where the pressure is *nil*, the boiling-point falls
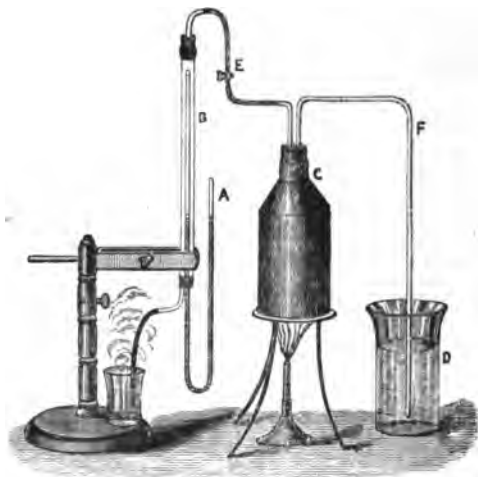
FIG. 21.—Tension of aqueous vapour.

below that at which water freezes. On the tops of mountains where the atmospheric pressure is comparatively low, water boils below 100°, while in steam boilers, where it is exposed to great pressure, the boiling-point rises to 144° with a steam pressure of 60 lbs. to the square inch (4 atmospheres) and to 180° at a pressure of 150 lbs.

58. Solution and Crystallization.—The fact has already been mentioned that water acts as a solvent of very many substances; it usually so acts more powerfully when hot (except with gases, which are more readily absorbed by cold water). Thus sodium sulphate is soluble in rather more than double its weight of water at usual temperatures;

whereas the salt may be dissolved without difficulty in its own weight of warm water.

Substances differ very greatly in their degree of solubility : they may be roughly classified into (1) freely soluble substances, as sugar, washing-soda, alum; (2) slightly soluble substances, as gypsum or plaster of Paris; (3) insoluble substances, as chalk, flint, and sand.

Experiment 55.—-Take half an ounce of sodium sulphate, place in a test-tube, and add the same weight of water; heat gently : the salt is dissolved. Now allow the solution to cool ; as the temperature falls the water is unable to hold the whole of the salt in solution, and a portion separates in the solid state, as a series of long four-sided prisms : these are *crystals* of sodium sulphate. At times in this experiment the solution may be cooled down without any crystals whatever separating. Should this be so, add the minutest particle of the dry sodium sulphate ; crystals will immediately separate.

Prepare crystals of sodium carbonate, and copper sulphate, in precisely the same manner.

A substance is said to be crystallised whenever it assumes a definite geometrical form ; the same substance, as a rule, always crystallizes in the same form or group of closely allied forms. When a body assumes two distinct crystalline forms it is said to be *dimorphous :* the study of even the more familiar elements includes some very important instances of dimorphism. A body which does not occur in crystals is termed *amorphous*, i.e. without (crystalline) form.

Many bodies require, in order to build up their crystals, a certain quantity of water; on removing this the crystalline form is destroyed.

Experiment 56.—Pour the contents of the sodium sulphate tube from the last experiment on a filter, so that the liquid may drain off (mother-liquor) ; dry the crystals by gently pressing them between the folds of a dry filter. Remove the dry crystals into a test-tube which is also dry, and very gently apply heat ;

the crystals melt, a quantity of water is given off, which con-
denses in the upper part of the tube, and ultimately a white,
solid, and amorphous mass remains at the bottom.

Such water is called *water of crystallization,* and is
always constant in quantity.   Thus, crystallized sodium
sulphate contains 10 molecules of water to one of the salt :
this is represented in the formula, Na_2SO_4, $10H_2O$.

59. Composition by Volume.—Water, until within
the last hundred years, was looked on as an element.   The
experiments described in the last chapter on hydrogen will
have shown the student that its composition is compound,
hydrogen having been obtained from it, and water again
produced by the combustion of that gas in air.

By intense heat water may be separated into oxygen
and hydrogen ; but the difficulty is that as the gases cool
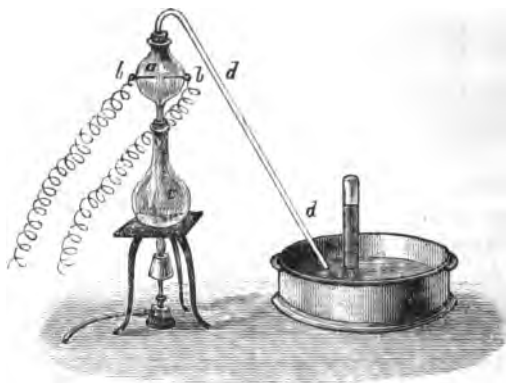
FIG. 22.—Decomposition of water by heat.

down, they once more combine and water is again pro-
duced.   The most convenient source of heat for the purpose
is that of the electric spark.

Experiment 57.—Procure a piece of apparatus consisting of
a glass bulb, *a*, Fig. 22, through which platinum wires, *b b*, are

fixed, so that their ends are in the centre of the bulbs and about an eighth of an inch apart. The lower part of this bulb, *a*, is provided with a glass tube, which must be passed through a cork fitted to the flask *c*. Fit a cork and leading tube, *d d*, to the top of the bulb *a*, and arrange a pneumatic trough for the collection of any evolved gases. Half fill the flask *c* with water; connect up the apparatus, and boil the water in *c* until the steam has expelled the whole of the air from the apparatus, the steam itself being condensed by the cold water in the trough. At this stage pass a series of sparks from an induction coil through the wires *b b*, and arrange a small stout gas-jar (explosion tube) to collect any gas escaping from *d d*. The passage of each spark decomposes a small quantity of steam, and, the mixed gases being immediately largely diluted with steam, some proportion at least is kept apart until the gases have cooled below their combining temperature. In this way the gas-jar is slowly filled with an explosive mixture of hydrogen and oxygen ; remove it from the trough, and apply a light— a violent explosion ensues.

The most convenient force to apply for the purpose of this decomposition, however, is that of voltaic electricity. The following series of experiments on the analysis of water by electricity (electrolysis) and its synthesis should, if possible, be performed by the student ; failing this, he should read the directions here given most carefully, and watch the results obtained when the experiments are performed by the teacher.

Experiment 58.—The electrolytic apparatus shown in Fig. 23 is to be attached by means of the wires to a battery consisting of two or three Grove's or Bunsen's cells. Such an apparatus is readily constructed by taking a wide-mouthed bottle, *a*, of 6 or 8 ozs. capacity, and fitting it with a good cork, through which passes the delivery tube *b*, and the necessary appliances for conveying a current of electricity to the contained liquid. For this purpose a very convenient arrangement consists of the glass tubes *c, c,* as shown in the figure. Into the lower ends of these are fused pieces of platinum wire to which small sheets of platinum foil, *d, d,* are attached. The tubes are then

to be filled with mercury, and the connection with the battery is easily made by pushing the *clean* ends of the wires into the liquid metal.

To use the apparatus, first fill the bottle to the neck with water, to which twenty or thirty drops of sulphuric acid have been added. Connect to the battery, and notice that a stream of bubbles of gas ascends from each piece of platinum. Collect the gas issuing from the leading tube in an egg-shaped soda-water bottle over the pneumatic trough. When full, close the
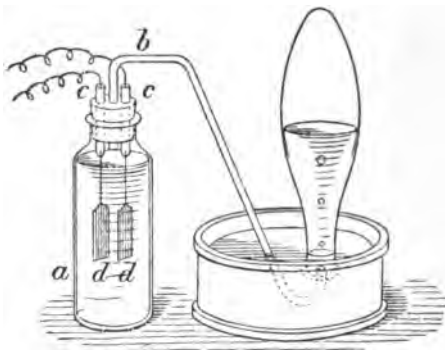
FIG. 23.—Electrolysis of water.

mouth either with a cork or the palm of the hand ; wrap up the bottle carefully in a duster and apply a light ; the gas explodes violently. Place the leading tube of the apparatus in a strong solution of soap, and thus blow some bubbles. Remove the apparatus and apply a light to the bubbles ; they detonate loudly.

The pieces of platinum foil are called *electrodes;* that connected with the zinc of the battery is the *negative*, the other the *positive* electrode.

Further information may be gained from a modified form of this experiment, in which the gas evolved from each of the electrodes is collected separately.

Experiment 59.—A convenient form of apparatus for this purpose is shown in Fig. 24, which consists of a shallow glass

vessel, v, containing acidulated water, and two electrodes connected to the binding screws s s. Fill the glass tubes with acidulated water, and invert one over each electrode. Connect the battery wires to the binding screws s s, to which the electrodes are attached. Gas immediately rises in each of the tubes ; it is soon noticed that in that inverted over the negative electrode the volume is double that evolved from the positive electrode. When nearly full, remove the inverted tube containing the larger quantity of gas and apply a light ; it burns quietly

FIG. 24.—Electrolysis of water.

with the familiar pale blue flame of hydrogen. In the second tube of gas plunge a glowing splinter; it re-lights, the gas being oxygen.

These experiments prove that **water is capable of decomposition into oxygen and hydrogen in the proportions of one volume of the former to two of the latter.** One circumstance about this experiment is at first somewhat puzzling: pure hydrogen is evolved at the one electrode, and pure oxygen at the other, while there is no sign of any transference of gas from the one to the other electrode
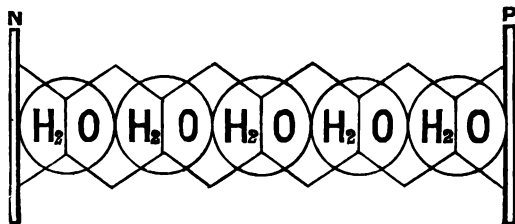
FIG. 25.—Diagrammatic representation of decomposition of water by electrolysis.

through the liquid. What, then, becomes of the oxygen which was in combination with the evolved hydrogen, and the hydrogen which was in combination with the evolved oxygen? This may best be explained by reference to the diagram given in Fig. 25, in which N and P are portions

H

respectively of the negative and positive electrodes of the apparatus shown in Fig. 24. The series of circles by which these are connected are intended to represent a line of molecules of water, making complete contact between the two electrodes. This is indicated by each containing the formula of water, H_2O. On the passage of an electric current, the molecule lying next to the negative electrode, N, is decomposed and its hydrogen liberated in the gaseous state. Its oxygen combines with the hydrogen of the next molecule to form water, and its hydrogen in turn decomposes the next adjoining molecule, until finally the molecule contiguous to the positive electrode, P, is reached; the oxygen there, finding no other molecule to decompose, is set at liberty, and escapes in the gaseous form. The formation of this second series of molecules is indicated in the diagram by the series of hexagons shown. If the electrode P be formed of any readily oxidizable metal, such as
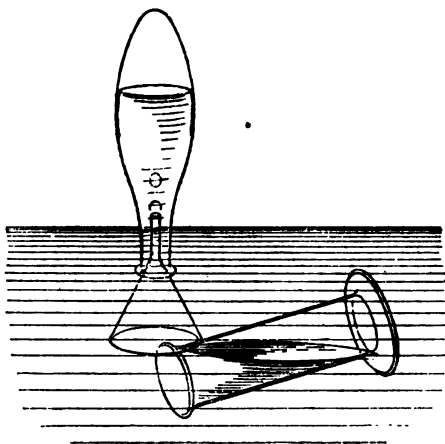
FIG. 26.— Transferring gases in the pneumatic trough.

zinc, the nascent oxygen combines with it to form an oxide, none escaping in the gaseous state.

The student should also learn that the reunion of oxygen and hydrogen again produces water.

Experiment 60.—Take the soda-water bottle used for the collection of the mixed gases in the electrolysis of water ; fill it with water, and pour out into a graduated measure; pour in again one-third of the quantity it holds, and mark the height by a file on the outside of the bottle ; pour in another third, and again make a mark. Now place the bottle in the trough, fill with water, and pour in, from a jar previously filled, one-third its volume of oxygen (Fig. 26). An easier way is to place the soda-water bottle on the beehive shelf, and place the mouth of the other underneath it ; or a funnel may be inverted in the mouth of the soda-water bottle. Next fill the remaining two-
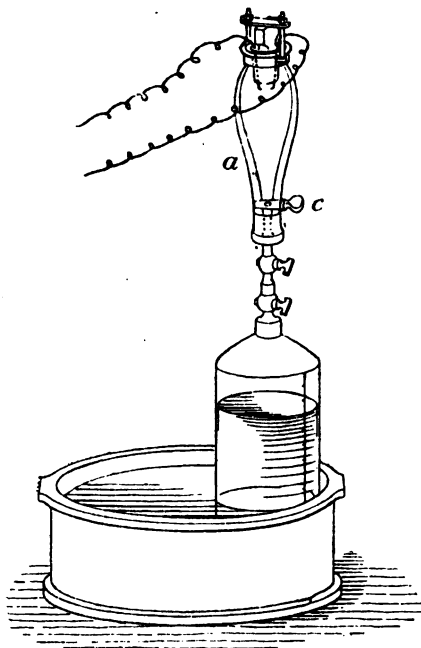
Fig. 27.—Combination of oxygen and hydrogen : Cavendish's experiment.

thirds of the bottle in the same way with hydrogen. Remove the bottle, give it one or two shakes, and, after wrapping in a duster or towel, apply a light; it explodes in just the same manner as the detonating gas collected by electrolysis.

The recombination of the two gases may be also effected by passing an electric spark through the mixture. Cavendish used in his investigations a strong glass vessel with two platinum wires inserted in it, so that the electric spark might pass through the gases between their ends. A form of his apparatus is shown in *a*, Fig. 27. This vessel is first exhausted by the air-pump, then attached to the graduated glass jar containing a mixture of two volumes of hydrogen and one of oxygen; on opening the stop-cock *c*, the vessel fills with the mixture. The stop-cock is closed and an electric spark passed; drops of water condense on the sides of the vessel. The stop-cocks may be again opened, and the vessel re-fills; by the passage of a spark a second quantity of water is produced. This operation may be repeated until the whole of the gases have been caused to combine; by this time there is an appreciable quantity of water in the glass vessel.

A somewhat similar experiment to this, but performed on a smaller scale, may be tried by the student himself.

Experiment 61.—For this experiment procure a *eudiometer tube* (Fig. 28).—This consists of a stout glass tube about 20 inches in length and half an inch

FIG. 28.—Combination of oxygen and hydrogen.

diameter, closed at one end. Near the closed end two platinum wires are fused into the glass, their points being about a sixteenth or eighth of an inch apart. Fill this tube with mercury, and invert in a small trough, also containing mercury, and provided with an indiarubber pad at the bottom. Fill the tube about one-third full of the mixed gases evolved by the apparatus in Fig. 23; attach the wires to a small induction coil or an electrophorus; hold the eudiometer down firmly on the rubber pad, and pass a spark through the gaseous mixture; there is a bright flash of light at the moment of
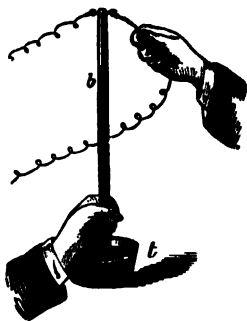
combination. Lift the tube slightly; the mercury rushes in and entirely fills it.

In this experiment the water vapour first formed immediately condenses. Another most important experiment, which the student should perform, if possible, consists of measuring the relative volume of the mixed gases, and the *steam* produced by their union.

The apparatus, usually described for this experiment, necessitates the use of means for maintaining the temperature of the eudiometer well above the boiling-point of water. Vapour of amylic alcohol, which boils at 132° C., is passed through an outer tube in which the eudiometer is placed. There is an elegant modification of this apparatus devised by Professor Reynolds, in which use is made of the fact that water boils at a lower temperature under less atmospheric pressure. The pressure on the water vapour inside the eudiometer being lessened, it is kept above its condensing temperature simply by the passage of steam through the outer tube.

FIG. 29.—Volumetric composition of steam.

Experiment 62.—Take a eudiometer tube about 30 inches long; place over it the jacket *j* (Fig. 29), which should be about 15 inches in length and an inch in diameter. Each end of the jacket is fitted with a cork; through the upper one a bent glass tube is passed, which is connected with the glass flask *f*, containing water heated by the Bunsen; *w w* the wires, also are passed through it, connecting the eudiometer with the induction coil. The lower cork has one hole which fits the eudiometer; through

a second the tube *t* is fixed for waste steam. Two small india-rubber rings should be passed over the outer jacket. Fill the eudiometer with mercury and invert it in a mercury trough with indiarubber pad *p* and a well *b*. Pass into it some of the electrolytic gases, about sufficient to one-third fill the tube ; do not let the quantity exceed this. Connect the flask *f* and pass a current of steam until the gases inside the eudiometer, expanding with the increased temperature, once more attain a constant volume. Mark this point by sliding the lower of the indiarubber rings to the surface of the mercury. Measure also and note the height of the mercury above the surface of that in the trough. Pass an electric spark, holding the eudiometer meanwhile firmly on the indiarubber pad ; the gas after com-bination is seen to decrease in volume ; as soon as stationary, depress the eudiometer in the well *b* until the mercury stands again the same height above the surface in the trough as when previously measured. Now place the second ring coincident with the surface of the mercury in the eudiometer. The amount of contraction thus measured will be found to be just one-third of the whole volume.

The current of steam must be maintained during the whole of the experiment. It may be found convenient to regulate the pressure by raising the mercury trough instead of lowering the eudiometer.

Three volumes of the mixed gases have produced two volumes of steam measured at the same temperature and pressure.

60. Composition by Weight.—The preceding series of experiments will have shown the student the com-position of water by volume; it is necessary that he should also be acquainted with the means employed for the deter-mination of the exact composition by weight. While iron and other metals decompose water, owing to their great attraction for oxygen, there is another group the oxides of which are decomposed by hydrogen, from their having a less powerful attraction or "affinity" for oxygen than hydrogen has for that element. As seen in a previous

experiment (No. 50), if oxide of copper be heated in a
current of hydrogen, water is produced and copper liberated
in the free state :—

$$CuO \quad + \quad H_2 \quad = \quad H_2O \quad + \quad Cu.$$

Oxide of copper.   Hydrogen.   Water.   Copper.
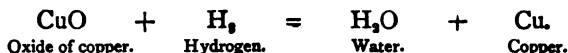
With proper precautions, this reaction enables us to
ascertain with exactness the relative weight of hydrogen and
oxygen which water contains.

Experiment 63.—Procure a piece of combustion tubing about
one foot in length, and with a bulb one inch in diameter blown
in the centre. Partly fill this bulb with clean dry copper filings,
and weigh the bulb and its contents. Pass a gentle current of
oxygen from a gas bag, or other holder, through the tube, and
heat the bulb to redness by means of a Bunsen. In about five
minutes disconnect the apparatus and weigh the bulb ; notice
that it has gained in weight. This is due to the formation of
copper oxide.

Next pass hydrogen over the copper oxide thus produced
and heat gently, using the same precautions as previously de-
scribed in a similar experiment. Notice the production of water
which drive out of the tube by slightly warming it through-
out its whole length. When no more water is being evolved,
cease the passage of hydrogen, allow the tube to cool, displace
any hydrogen it may contain by passing a current of air
through, and again weigh the tube. The weight is the same
as that of the tube originally, showing that the oxide is again
reduced to the metallic state.

In order to utilize this chemical change for the determi-
nation of the relative proportions by weight of hydrogen
and oxygen in water, the following modification of this
experiment may be adopted :—

Experiment 64.—Fit up the apparatus shown in Fig. 30 by
preparing first a generating flask or bottle, A, in which hydrogen
is evolved by the action of zinc and sulphuric acid. Attach
this to the wash-bottle B, in which place a solution of caustic
potash in order to retain any traces of sulphuric acid that may
be carried over mechanically. Fit up the tubes C, D, E with

corks and leading tubes, so that the gas may be conducted through the whole series. Fill C and E with fragments of pumice ; moisten that in C with a solution of mercuric chloride ($HgCl_2$), and that in E with strong sulphuric acid. Fill D with fragments of fused potash. The passage of the gas through the
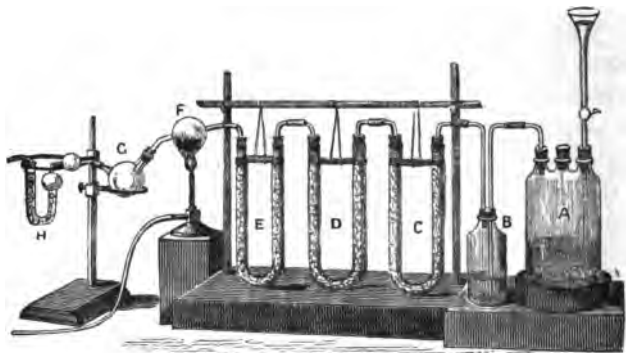
FIG. 30.—Composition by weight of water.

wash-bottle and these tubes removes all impurities, *dry* hydrogen only escaping from E. The globe F is a bulb blown on a piece of combustion tubing ; attach this to E by indiarubber tubing, and so arrange that a Bunsen may be placed underneath it. Arrange the bulb G for the collection of water, and for H obtain a drying tube and fill it with fragments of calcium chloride.

Having the rest of the apparatus in readiness, introduce about half an ounce of dry copper oxide in F and weigh accurately. Also weigh both G and H. Connect up the apparatus by indiarubber tubing and see that the joints are air-tight. By the addition of a small quantity of sulphuric acid to A, cause a slow evolution of hydrogen ; allow this to expel the whole of the air from the apparatus and then gently heat the oxide of copper by means of the Bunsen under F ; notice that water is formed, and collects in the receiver G ; any traces of vapour are retained by the calcium chloride in H. In about ten minutes remove the Bunsen and allow the bulb to cool ; disconnect the hydrogen apparatus A, and draw air through the tubes in order to displace the hydrogen. Weigh the copper oxide globe ; the loss represents the oxygen which has combined with hydrogen

to form water. Weigh also G and H; their combined increase in weight is the weight of water which has been produced.

Supposing as the result of an actual experiment that the oxide of copper has lost 16 decigrammes of oxygen, the receiver and drying tube will be found to have gained 18 decigrammes in weight. We know, therefore, that water contains (very nearly) 16 parts by weight of oxygen and 2 parts by weight of hydrogen in 18 parts of water, or 8 parts by weight of oxygen to 1 part by weight of hydrogen.

61. Hydrogen Dioxide, or Hydroxyl. — This second compound of hydrogen and oxygen differs from water in that it contains an extra atom of oxygen in the molecule; the second atom is, however, held somewhat loosely; hence this body is readily decomposed into water and free oxygen.

For a description of hydroxyl the student is referred to one of the larger treatises on Chemistry.

Summary.

Water is a widely distributed liquid ; from its solvent powers it is never found pure. Heat changes its condition from solid to liquid and liquid to gas. The boiling-point depends on pressure. Many crystals contain water as an essential constituent. Is decomposed by electricity into an explosive mixture of gases ; each may be collected separately ; the gases re-combine to again form water. By volume water consists of two volumes of hydrogen and one of oxygen, which condense on union to form two volumes of steam. By weight water contains sixteen parts of oxygen to two of hydrogen.

OBJECT DEMONSTRATION.

Observe the nature and shape of the crystals of sodium sulphate in experiment 56. Compare them with potassium chlorate, and other chemical bodies which have been used in previous experiments. Also, if practicable, examine some typical crystalline specimens of minerals, and models of crystals.

LABORATORY DIRECTIONS.

In this chapter a description is given of many experiments which are usually performed on the lecture-table, and not by each student. Observe each of these very carefully, compare the apparatus with the description given, and note the results obtained. Fix in the mind the exact lesson each of these experiments is intended to convey.

The U tube with jacket and eudiometer for the experiments of this chapter may be obtained from the general apparatus of the laboratory. The boiling-flask shown in Fig. 21 is fitted with a safety tube, F, which provides for the exit of steam until required to pass through the apparatus. The beaker D is nearly filled with water. When the screw-tap E is closed the steam must perforce adopt that way of escape; but if the tap be opened the steam passes through the apparatus in preference to forcing itself through some four or five inches of water in the beaker. This device may be dispensed with in this particular experiment, but frequently is of great use where a current of steam is required to be carefully regulated or alternately shut off and re-admitted.

In working with mercury, take care that none is lost. Failing a proper bench with a ledge round it, it is better to stand the whole apparatus in a shallow drawer or tray. Dirty mercury may be cleaned by folding a piece of writing-paper as a filter and placing it in a funnel. Prick two or three holes with a pin through the bottom; pour in the mercury: it runs through perfectly bright and clean. To fill a U tube, pour in as much mercury as it will hold ; then close the open end with the thumb ; and turn it over : the mercury will run into the sealed limb. If necessary, turn it upright, pour in some more mercury, and turn flat : in this way the tube may be filled.

In the sodium sulphate experiment it is possible that when the liquid is cooled no crystals will separate. If this be the case, throw in a single small crystal of the salt : around this as a nucleus the crystals will rapidly form.

An electric battery of three or four of either Grove's or Bunsen's cells is most suitable for the decomposition of water; the only difference between these forms of battery is that Grove employs as the positive element a sheet of platinum foil ; while Bunsen uses a rod of carbon. To use the battery, first see that

the zinc plates are bright all over with mercury; if this is not
the case, they should be re-amalgamated. Dip each plate in a
dilute solution of sulphuric acid (1 of acid to 10 of water); after
half a minute remove the plate, pour a little mercury on it, and
rub over every part with a piece of flannel tied on to the end of
a stick until the whole surface of the zinc is bright with a coating
of mercury. Place the zincs in the outer cells with the ends to
which the binding screws are attached, all looking the same
way; put in the porous cells, and the platinum foil again inside
the porous cell. Connect the end zinc of all to the conducting
wire by means of a binding screw; connect together the
platinum of that cell and the zinc of the next with a binding
screw, letting the screw be on the zinc side and the flat part of
the connection against the platinum. The platinum and zinc of
each of the adjoining cells must be thus connected; the end
platinum must have the second wire attached to it. At the end
of the box in which the cells are supplied, there is a piece of
sheet vulcanite, against which the platinum is fixed. All the
connections, wires, etc., must be perfectly clean and bright.
Next fill the porous cells by the aid of a funnel with the strongest
commercial nitric acid, taking care that none overflows. The
outer cells are to be filled with sulphuric acid of the same
strength as that used to amalgamate the zincs. When the
battery is finished with, unscrew the connections, wash the bind-
ing screws in a stream of water, and wipe dry with a duster.
Pour the nitric acid back into a bottle kept for the purpose.
The sulphuric acid may, as a rule, be thrown away; if used for
only a few minutes, it may, however, be employed once again.
Rinse the porous cells and other parts thoroughly; before
putting away, the porous cells will be all the better for soaking
in clean water for a few hours. Always keep them full of water
when not in use.

The most convenient apparatus for the production of an
electric spark is a small induction coil. This is conveniently
worked by a single bichromate cell; the advantage of this
is that the cell is kept charged, the zinc being simply lifted out
of the liquid. When required for use, connect by means of
wires to the coil; connect also the terminals of the secondary
circuit to the eudiometer; before filling it with gas, see that all
is in working order; lower the zinc of the cell in the acid,
tighten the binding screw, and turn on the current by means of

the screw or handle fixed for that purpose on the coil ; a rapid series of sparks should pass between the ends of the wires in the eudiometer.   Do not let the zinc remain in the acid longer than necessary for the experiment.

In using ether, take care to keep any light at a distance ; also replace the stopper and put the bottle in its proper place immediately.   Ether is very volatile and very inflammable.

In Exp. 53 the reason for filling the leading tube with water is to lessen the amount of air which is mixed with the small quantity of gas given óff.   An easy way to do this is to attach some indiarubber tubing to the end of the leading tube ; suck water into it from the trough or a beaker, and when full pinch the rubber tubing, fit the cork to the tube, and allow the end to remain under the water in the trough.

CHAPTER VII.

CHLORINE.

Symbol, Cl. Atomic weight, 35·37. Density, 35·37. Specific gravity, 2·435. Molecular weight, Cl_2, 70·74. Melting-point, $-102°$ C. Boiling-point, $-33·6°$ C. at atmospheric pressure.

62. Occurrence.—This gas is not known in the free state in nature, but occurs in vast quantities in combination with sodium, forming rock salt.

63. Preparation.—This gas may be readily obtained from its compound with hydrogen (hydrochloric acid, HCl) by the action of manganese dioxide; on mixing these substances together a compound of chlorine with manganese is formed thus:—

$$4HCl \quad + \quad MnO_2 \quad = \quad MnCl_4 \quad + \quad 2H_2O.$$
Hydrochloric   Manganese   Manganese   Water.
acid.   dioxide.   tetrachloride.
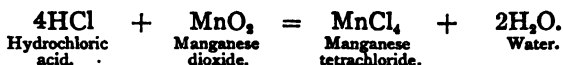
The manganese tetrachloride is an unstable compound, and, with an elevation of temperature, is decomposed into a chloride containing half the amount of chlorine, with the separation of the remainder in the free state—

$$MnCl_4 \quad = \quad MnCl_2 \quad + \quad Cl_2.$$
Manganese   Manganese   Chlorine.
tetrachloride.   dichloride.

In the actual preparation of the gas these two actions go on together, the tetrachloride being decomposed as rapidly as formed. Chlorine is manufactured in large

quantities by this process for various uses in the arts. Chlorine is sometimes prepared from common salt (sodium chloride) direct, by the action on it of manganese dioxide and sulphuric acid : the gas is disengaged in the cold, but more rapidly with the application of heat. The whole of the chlorine is liberated—

$$2NaCl \quad + \quad 3H_2SO_4 \quad + \quad MnO_2 \quad =$$

<div align="center">Sodium   Sulphuric acid.   Manganese
chloride.   dioxide.</div>

$$2NaHSO_4 \quad + \quad MnSO_4 \quad + \quad Cl_2 \quad + \quad 2H_2O.$$

<div align="center">Hydrogen sodium   Manganese   Chlorine.   Water.
sulphate.   sulphate.</div>
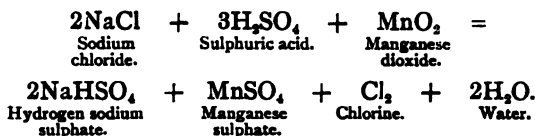
Chlorine may also be obtained by the electrolysis of a solution of hydrochloric acid.

For the study of the properties of chlorine the gas may be prepared from hydrochloric acid and manganese dioxide.

Experiment 65.—Take the apparatus No. 1, consisting of a 16-oz. flask, fitted with thistle funnel and leading tube. Pour into the flask sufficient strong commercial hydrochloric acid, to just cover the bottom ; then add about an ounce of powdered manganese dioxide; next pour in 3 or 4 oz. of the hydrochloric acid, and shake the mixture well up ; fix in the retort stand and introduce the cork. Fig. 32, *a*, is a flask arranged for the preparation of chlorine. The gas, being soluble in rather less than half its volume of cold water, cannot well be collected over that liquid. The process of downward displacement must be employed, or the water used must be hot. Eight jars of the gas will be required for the following experiments ; it will be, as a rule, convenient to fill the jars twice. Having the four jars and well-greased plates ready, proceed to collect over hot water, if obtainable ; if not, by downward displacement. In the latter case, the colour of the gas will indicate when the jars are full. Light the Bunsen and apply a gentle heat ; the gas is readily disengaged. Having filled three bottles, remove the Bunsen, and the action will almost cease until the flame is reapplied. Under any circumstances, take care that as little gas as possible escapes in the room. Where possible, chlorine should be made in a stink-closet—*i.e.* a closet provided with a sliding glass door and flue for the removal of obnoxious gases.

If there is no other alternative but to make it in the open laboratory, have every window possible open. It must be remembered ·that when a flask is heated, a piece of wire gauze is to be interposed between it and the flame.

64. Properties.—*Experiment* 66.—Introduce into one jar a lighted taper : the gas does not take fire ; the taper continues burning, but with a dull, smoky flame. Notice that, in addition to the soot, there is an abundance of white fumes produced.

Experiment 67.—Put a small piece of phosphorus in a deflagrating spoon, and, without lighting it, place in a jar of the gas ; notice that it commences to burn spontaneously, but does not evolve a very bright light.

Experiment 68.—Powder very finely some metallic antimony and drop a pinch into a bottle of the gas ; it immediately takes fire. Into another jar drop a sheet of thin copper foil,. or else a leaf of Dutch metal (a mixture of copper and zinc) ; it also immediately takes fire.

For two of the following experiments dry jars are required ; they must, therefore, be wiped dry with the duster and filled by displacement :—

Experiment 69.—Take a small piece of sodium in a *dry* and clean deflagrating spoon ; heat in the Bunsen flame until it is quite melted ; plunge it in the *dry* jar of gas : it burns with the production of great heat, and white fumes of common salt are deposited.

Experiment 70.—Take the other dry jar of gas and introduce into it a piece of *dry* red cloth or blotting-paper. Notice that the colour does not disappear.

Next pour into the jar of gas a solution of some vegetable colouring matter, as litmus or indigo ; shake up : the colour is instantly destroyed, and cannot be restored. Introduce also a moistened piece of red blotting-paper : the colour is discharged. It will be observed that the presence of water is necessary in order that the operation of bleaching may proceed.

Experiment 71.—Fit up the 8-oz. flask for the generation of hydrogen from zinc and sulphuric acid ; attach to it a jet thus (Fig. 31), with a piece of indiarubber tubing. After taking the usual precautions, light the jet and introduce it into a jar of chlorine ; notice that the gas continues to burn, and

that copious fumes are formed.   At the same time the yellow tint due to chlorine disappears.

The affinity of hydrogen and chlorine for each other is so great that many organic bodies containing hydrogen are decomposed by chlorine gas.

FIG. 31.—Burning hydrogen in chlorine.

Experiment 72.— Take a piece of tow, pull it out as loose as possible, wet with turpentine (a hydrocarbon with the formula $C_{10}H_{16}$) ; drop this into a jar of chlorine ; it is decomposed, usually with heat and light.   The carbon is deposited as soot ; the hydrogen again produces fumes of hydrochloric acid.

The student will now have verified many of the properties of this gas for himself in the preceding experiments. Chlorine is of a yellowish-green colour, and has a most pungent and disagreeable odour, which, when much diluted with air, somewhat resembles that of seaweed.   It acts as an irritant poison when in the pure state, or even when present in considerable quantity in air.

It is soluble in cold water, which, at a temperature of 15° C., dissolves 2·368 volumes of the gas.   Chlorine can be liquefied by a pressure of six atmospheres at 0° C., and solidifies at a temperature of − 102° C. at atmospheric pressure.

Experiment 73.—Pass some chlorine from the gas-evolving apparatus for some time into water.   Note that the gas imparts a yellow tint to the water, which at the same time acquires the characteristic odour of chlorine.

Add a little of this chlorine solution to solutions of litmus and indigo ; notice that the solution possesses the same bleaching properties as the gas.

Add some of the chlorine solution to silver nitrate solution ; a white precipitate of silver chloride is formed.

To solutions respectively of potassium bromide and iodide, add clorine solution ; notice that in each case a deep coloration is produced, which is due to the liberation of bromine or iodine. To prove the presence of free iodine in the potassium iodide solution, add a few drops of a solution of starch, when the characteristic deep blue coloration is produced. If wished, the potassium iodide and starch solutions may be mixed prior to the addition of the chlorine.

Like oxygen, chlorine supports combustion, and is non-inflammable; it is a most active element, forming bodies called chlorides with the whole of the elements. It has a remarkable affinity for hydrogen; on exposing a mixture of those gases to diffused daylight, they slowly combine : bright sunlight effects their immediate union with explosion. Intense artificial light, such as that of burning magnesium, produces the same effect. Carbon does not burn in chlorine, and if bodies containing it are burned, the carbon is deposited in the free state. One important peculiarity of the combustion of bodies in chlorine is that they often spontaneously ignite. As a rule, although a lower temperature is sufficient for the commencement of the formation of chlorides, the heat evolved during the union is less than that evolved in the production of the corresponding oxides.

The chemical actions occurring in the previous experiments are represented in the following equations :—

$$P_4 \quad + \quad 10Cl_2 \quad = \quad 4PCl_5.$$
Phosphorus.   Chlorine.   Phosphorus pentachloride.

$$2Sb \quad + \quad 5Cl_2 \quad = \quad 2SbCl_5.$$
Antimony.   Chlorine.   Antimony pentachloride.

$$2Na \quad + \quad Cl_2 \quad = \quad 2NaCl.$$
Sodium.   Chlorine.   Sodium chloride.

$$H_2 \quad + \quad Cl_2 \quad = \quad 2HCl.$$
Hydrogen.   Chlorine.   Hydrochloric acid.

$$C_{10}H_{16} \quad + \quad 8Cl_2 \quad = \quad 16HCl \quad + \quad 10C.$$
Turpentine.   Chlorine.   Hydrochloric acid.   Carbon.

I
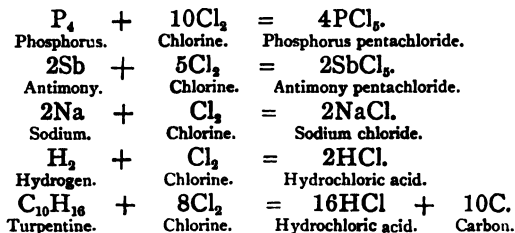
Water must be added to the list of hydrogen compounds capable of decomposition by chlorine. If a solution of chlorine in water is exposed to the sun's rays, bubbles are seen to rise to the surface, which, on examination, are found to be oxygen. At the same time the solution loses its yellow colour. The experiment is best performed by inverting a gas-jar filled with the solution in a small trough also containing saturated chlorine water. At a higher temperature the decomposition takes place more rapidly.

Experiment 74.—Connect a flask, *a*, Fig. 32, fitted for the preparation of chlorine, to the second flask, *b*, which contains water ; the leading tube from *a* dipping beneath the water-leveL Through the gas-tube furnace pass a porcelain tube, *c c*, filled with fragments of porcelain or flint, and fitted at each end with
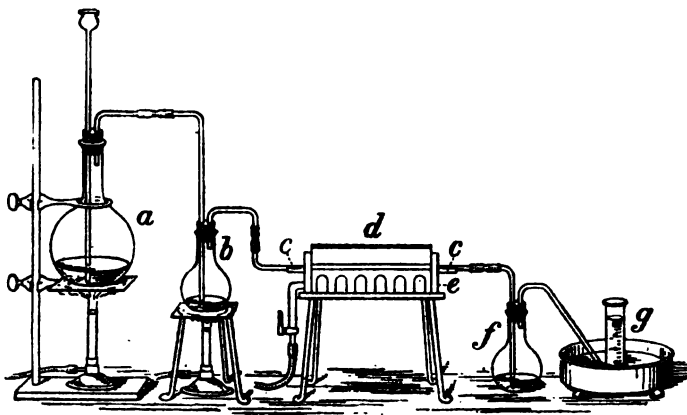
Fig. 32.—Decomposition of water by chlorine.

corks and glass tubes. The danger of cracking the porcelain tube is lessened by placing it in a semicircular iron trough, *e*, just large enough for the tube to lie in. This is conveniently made from a piece of sheet iron, which can readily be turned up into a semicircle one inch internal diameter by any smith. The flask *f* is a wash-bottle, containing a solution of caustic potash, for the purpose of removing the hydrochloric acid and any excess

of chlorine ; the oxygen passes over, and is collected in the jar *g*. The tubes *b* and *f* are connected to the porcelain tube by india-rubber tubing. The furnace must first be lighted and the tube raised to redness ; then light the Bunsens under both the chlorine and water flasks : a mixture of chlorine and steam enters the furnace, decomposition ensues, and oxygen and hydrochloric acid escape.

The reaction is thus represented :—

$$2Cl_2 \quad + \quad 2H_2O \quad = \quad 4HCl \quad + \quad O_2$$
Chlorine.   Water.   Hydrochloric acid.   Oxygen.
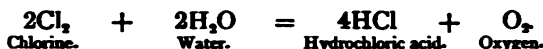
This experiment is an important one, as showing the presence of oxygen in water ; unlike hydrogen, by no known means can the oxygen of water be displaced in two instalments.

Chlorine is one of the most powerful bleaching or de-colorising agents known ; there are few vegetable colouring matters which are unattacked by it : ink, litmus, etc., are rapidly changed into colourless bodies. Mineral ink or printers' ink is not changed. Chlorine has no bleaching action in the absence of water ; in its presence that com-pound is decomposed with the formation of hydrochloric acid. The nascent oxygen combines with the colouring matter and produces a compound containing a higher pro-portion of oxygen, and devoid of colour. Free oxygen has little, if any, bleaching power.

Chlorine decomposes silver nitrate with the formation of insoluble silver chloride, and hence causes a precipitate in a solution of a silver salt.

The action of chlorine on bromides and iodides is another instance of the great activity of this element. The following equations represent the chemical changes which occur :—

$$Cl_2 \quad + \quad 2KBr \quad = \quad Br_2 \quad + \quad 2KCl.$$
Chlorine.   Potassium bromide.   Bromine.   Potassium chloride.

$$Cl_2 \quad + \quad 2KI \quad = \quad I_2 \quad + \quad 2KCl.$$
Chlorine.   Potassium iodide.   Iodine.   Potassium chloride.
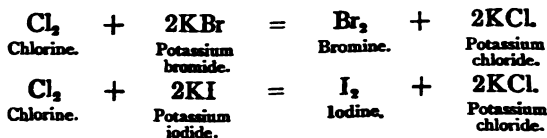
These reactions will be examined more fully when the elements bromine and iodine are under consideration.

Summary.

Chlorine is a heavy gas; does not occur in nature in the free state, but largely in combination with sodium. May be obtained from either hydrochloric acid or sodium chloride, or by electrolysis of hydrochloric acid. Possesses a yellow-green colour; odour somewhat like seaweed, and acrid taste; non-inflammable; supports combustion; soluble in water; is a powerful bleaching agent; decomposes water with evolution of free oxygen.

OBJECT DEMONSTRATION.

Note the appearance of metallic antimony, and at the same time its extreme brittleness.

Compare the elements bromine and iodine with chlorine, both in the pure state and in solution in water. Bromine is a liquid, and iodine a solid. The aqueous solutions of each somewhat resemble each other in colour and also in smell.

LABORATORY DIRECTIONS.

Chlorine rapidly attacks corks; they may be protected by dipping them into melted paraffin; not *paraffin oil*, but the solid substance melted in a small dish or pipkin. The reason for *first* adding hydrochloric acid, subsequently the manganese dioxide, and shaking up so thoroughly, is that otherwise the oxide is liable to form a cake at the bottom : this gets hot, and the liquid, finding its way through it after a time, cracks the vessel.

The fumes produced by burning both phosphorus and antimony in chlorine are poisonous, and should not be breathed.

The reason why such care must be taken to have dry jars for sodium experiments is that hot sodium accidentally coming in contact with water explodes violently. See also that there is no water spilled about the working bench. For the hydrogen experiment a second generating apparatus is required; a second thistle funnel is a useful addition to the apparatus list given on

page 19. Failing this, all other experiments with chlorine may be first tried, and then the apparatus cleaned and used for hydrogen. In the last experiment there is considerable danger of breaking the porcelain tube ; it is a good plan to incline it a little, so that the steam in passing through it has to rise ; this prevents any condensed steam running on to the red-hot porcelain. When the experiment is finished, disconnect the other apparatus, and allow the tube to cool slowly in the furnace.

Wash all apparatus used for chlorine immediately it is finished with ; this applies especially to corks and indiarubber tubing : the latter should have a stream of water sent through it.

CHAPTER VIII.

HYDROCHLORIC ACID.

Formula, HCl. Molecular weight, 36·37. Density, 18·18. Specific gravity, 1·2474. Melting-point, − 112·5° C. Boiling-point, 10° C. under a pressure of 40 atmospheres.

65. Occurrence.—At ordinary temperatures hydrochloric acid is a gas, and is found in small quantities in the gaseous mixture evolved from volcanoes. This compound has also received the name of muriatic acid (from *muria*, brine), and is the only known compound of hydrogen and chlorine. Its preparation by the direct union of these elements has already been described.

66. Preparation.—The gas is easily obtained by the action of sulphuric acid on almost any chloride; because of its cheapness, common salt is usually employed. Salt in its ordinary form is so finely divided that the action proceeds with almost unmanageable rapidity. This may be modified by first fusing the salt and then breaking the solid mass thus obtained into small lumps. The gas is extremely soluble in water, and therefore has to be collected by downward displacement.

The reaction is represented by the following equation:—

$$H_2SO_4 \quad + \quad NaCl \quad = \quad NaHSO_4 \quad + \quad HCl.$$

Sulphuric acid.   Sodium chloride.   Hydrogen sodium sulphate.   Hydrochloric acid.
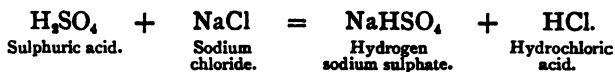
One atom of the hydrogen of the sulphuric acid is here driven out by the sodium. At a much higher temperature

than could be used with a glass flask, the second atom of hydrogen is displaced :—

$$NaHSO_4 \quad + \quad NaCl \quad = \quad Na_2SO_4 \quad + \quad HCl.$$

Hydrogen sodium   Sodium   Sodium   Hydrochloric
sulphate.   chloride.   sulphate.   acid.
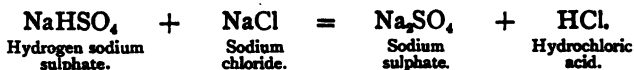
Experiment 75.—Fill a clay crucible about 5 inches in height with common salt; melt over a bright red fire or in a furnace, and pour the molten mass on to a cold iron plate. When cold, break up and store in a bottle, which must be kept corked. Place about half an ounce of the fused salt in the generating flask, with funnel and leading tube arranged for downward displacement; see that the indiarubber and other tubes are dry. Fix in the retort stand, and pour in sufficient concentrated sulphuric acid to cover the salt : the gas is evolved rapidly even in the cold. Thoroughly dry four gas-jars, and fill them ; should the evolution of gas slacken, apply heat. Copious fumes emerge from the mouths of the jars as soon as full. Next place the delivery tube in a beaker, into which exactly 100 c.c. of water have been poured ; notice that the gas is absorbed as rapidly as formed, and that the water rises in temperature. After some minutes, pour the solution back into a measuring tube. The volume will have increased.

67. Properties.—*Experiment* 76.—Take the plate off one jar of gas ; observe that, although the gas itself is clear, the fumes seen so frequently before again make their appearance when the gas comes in contact with the air. Introduce a lighted taper : the taper is extinguished, and the gas itself does not light.

Experiment 77.—Place the mouth of the second jar under-water, and slide off the glass plate ; the water rapidly fills the jar.

Experiment 78.—To the third jar add some litmus solution, and shake up ; the colour is seen immediately to change to red.

Experiment 79.—Into another jar of gas hold a piece of paper which has been dipped in a concentrated solution of ammonia ; observe the production of dense white fumes of ammonium chloride.

Experiment 80.—Examine now the solution made by passing the gas into water ; it possesses the odour of the gas, evolves pungent fumes, and, like it, immediately reddens litmus.

Add some of the aqueous solution of the gas to litmus solution ; notice that the colour changes to red, but that no bleaching action results.

Add a portion of the solution of the gas to silver nitrate solution ; a white curdy precipitate of silver chloride is formed.

Add some of the hydrochloric acid solution to a mixture of potassium iodide and starch solutions ; no coloration is produced, showing that hydrochloric acid does not liberate iodine from its compounds.

In common with water, hydrochloric acid gas is decomposed by iron at a red heat, with the evolution of hydrogen.

Experiment 81.—Fit up the apparatus, consisting of iron tube containing filings as shown in Fig. 19, except that a hydrochloric acid generating apparatus is substituted for the steam-flask. Pass the gas over the iron turnings, and collect and test the hydrogen.

The following equation represents the change which occurs :—

$$\underset{\text{Hydrochloric acid.}}{\text{HCl}} \quad + \quad \underset{\text{Iron.}}{\text{Fe}} \quad = \quad \underset{\text{Iron chloride.}}{\text{FeCl}_2} \quad + \quad \underset{\text{Hydrogen.}}{\text{H}_2}$$
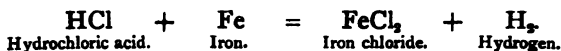
The same reaction takes place when iron is added to a concentrated solution of hydrochloric acid gas in water. Zinc and other easily oxidized metals displace the hydrogen in a similar manner.

Hydrochloric acid is colourless, but is rendered visible on coming in contact with air containing moisture by the formation of a compound with water which condenses to liquid globules; hence the dense fumes so often noticed. It has a sharp, pungent odour ; its solution in water is intensely sour, and reddens litmus solution ; it is a very powerful acid, and forms an important series of salts known as chlorides. Water at 15° C. dissolves 454 volumes of hydrochloric acid.

Hydrochloric acid in the gaseous form is distinguished

by the dense fumes it forms with ammonia. In solution it produces a characteristic precipitate of silver chloride from the nitrate. It shares this property with the soluble chlorides, and also as shown by experiment with a solution of chlorine. It is distinguished from this gas by its having no bleaching power, and being without action on a solution of potassium iodide and starch.

68. Composition.—The composition of the gas may be ascertained by exposing its solution to electrolysis, when it is resolved into equal volumes of hydrogen and chlorine.

The best apparatus to use for this experiment is Hofmann's, which, as shown in Fig. 33, consists of three tubes, connected at the bottom; through A and B are passed indiarubber corks with carbon electrodes (platinum cannot be used, as that metal is attacked by nascent chlorine).

Experiment 82. — Fill the apparatus with concentrated hydrochloric acid just to the level of the stop-cocks, leaving them open; connect with a battery of three or four cells, and allow the current to pass for an hour; the hydrogen
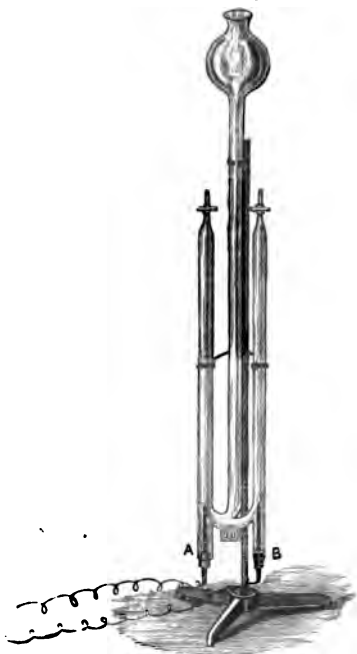
FIG. 33.—Electrolysis of hydrochloric acid.

rises rapidly from the negative electrode, but, from chlorine being soluble in water, little gas is evolved until the solution is saturated. At the end of this time, turn off the stop-cocks; equal volumes of gas should collect in each tube. Should the chlorine

be in too small a quantity, it is a sign that the acid in that limb is not yet saturated. The chlorine may be recognized by its colour ; open the stop-cock and let the gas impinge on a piece of wet litmus paper ; the colour of the litmus is discharged. Connect a small glass jet to the limb containing hydrogen by indiarubber tubing ; open the stop-cock and apply a light to the issuing gas, which is recognized by its inflammability.

Chlorine, like oxygen, is liberated from the electrode connected with the copper or platinum element of the battery. The following eight elements are alike in this respect, and from their behaviour with an electric current are called negative :—oxygen, chlorine, bromine, iodine, fluorine, sulphur, selenium, and tellurium.

In the event of the apparatus for performing the last experiment not being obtainable, the presence of both chlorine and hydrogen in hydrochloric acid may be detected in the following manner :—

Experiment 83.—Fit to the generating flask *a* (Fig. 34), containing salt and sulphuric acid, a U tube, *b*, containing
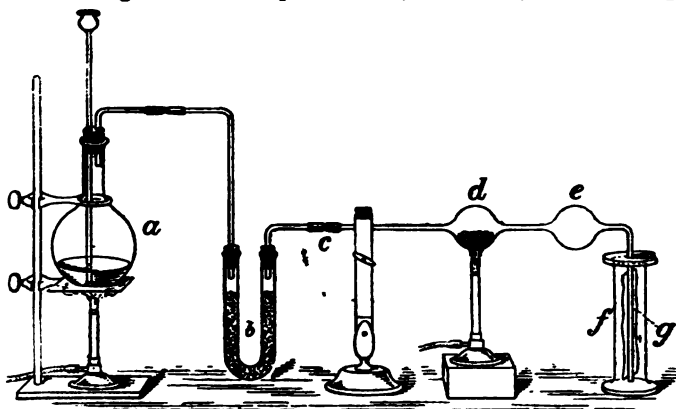
FIG. 34.—Composition of hydrochloric acid.

calcium chloride for drying the evolved gas. Connect this to a tube in which two bulbs (*d, e*) have been blown : in the first of

these place some powdered manganese dioxide, which has been thoroughly dried by warming in an iron ladle over the Bunsen flame. Arrange a glass jar, *f*, to receive the escaping gas; place in it a sheet, *g*, of moist blue litmus paper. The hydrochloric acid evolved at once changes the colour. Apply heat to the bulb containing manganese dioxide; the hydrochloric acid is decomposed; water collects in the second bulb, *e;* chlorine passes over into the jar, and is recognized by its odour and bleaching power.

The composition of hydrochloric acid by synthesis is shown by the explosion of hydrogen and chlorine in equal volumes in a specially constructed tube. The gases for the purpose are conveniently prepared by electrolysis; or working by gas or diffused daylight, they may be mixed in a bottle over saturated chlorine water in a small trough or beaker, and then transferred to the explosion tube: this simply consists of a glass tube about twenty inches in length, with a stop-cock at each end, and two platinum electrodes fused through the middle.

Experiment 84.—Procure a small gas-jar, *a* (Fig. 35), open at top and bottom; one holding 20 or 32 oz. is a convenient size. Close the upper opening with a cork which has been dipped in melted paraffin. Bore a hole and pass through it a glass tube with stop-cock. Failing this, a plain glass tube with a piece of indiarubber tubing and a pinch-cock may be used. Turn the jar *a* bottom upwards and exactly upright, and proceed to graduate it by pouring in successive quantities of 25 or 50 c.c. of water, making a mark at the level of each on the outside of the jar either with a sharp file or a writing-diamond. These marks should be numbered 1, 2, 3, etc., from the top of the jar downward. Having prepared the jar, stand it in a small trough or large glass beaker, filled with saturated chlorine water; pass the indiarubber tubing over *b*, allow the air to escape from the jars, and close the screw-tap; next introduce through *b* 200 c.c. of hydrogen, and then the same quantity of chlorine, and agitate the jar, so as to mix the gases. Connect the glass tube *b* with the small U tube *c*, filled with calcium chloride, and attach the explosion tube *d* to the

second end of the U tube. Open the whole of the stop-cocks sufficiently for the weight of the jar *a* to force the mixed gases *slowly* up into and through *d*. When nearly the whole of the gas has been allowed to escape, close the stop-cocks; *d* is now filled with a mixture of equal volumes of hydrogen and chlorine, which has expelled the air. Attach the wires *e e* from
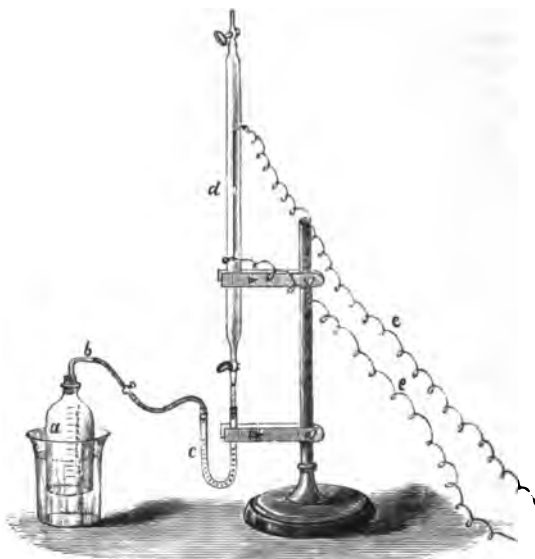
FIG. 35.—Composition of hydrochloric acid gas.

the induction coil to the electrodes, and pass an electric spark : combination takes place between the gases. When they have cooled down to the original temperature, place one end of the explosion-tube under the surface of mercury, and open the stop-cock; the mercury does not rise, showing that there is no alteration in the volume of the gas. Remove and open the stop-cock with the end immersed in water ; the water rushes up and fills the whole of the tube.

These experiments show that hydrochloric acid is a gas produced by the union of equal volumes of hydrogen and chlorine without condensation. The composition by weight

may be demonstrated by means similar in principle to those adopted in the case of water.

Summary.

Hydrochloric acid is the only compound known of hydrogen and chlorine ; may be easily prepared by the action of sulphuric acid on a chloride. The gas is very soluble in water ; is colourless, but fumes on exposure to air ; has a sharp, pungent odour and sour taste ; is non-inflammable and a non-supporter of combustion ; reddens litmus. Is composed of equal volumes of hydrogen and chlorine united without condensation ; this is proved both by analysis and synthesis.

OBJECT DEMONSTRATION.

Note the appearance of fused salt; compare same, if possible, with that of rock-salt.

LABORATORY DIRECTIONS.

Fused salt is as a rule kept in a laboratory ; it is a convenient plan to get a working jeweller to melt down a good stock in one of the large crucibles used in the trade : the cost for melting would not be excessive.

It is not absolutely necessary, in Exp. 83, that the tube containing manganese dioxide should have bulbs blown on it ; bending it in the form of a W answers the purpose.

The graduated jar and explosion tube for Exp. 84 will, in most cases, be found among the general apparatus of the laboratory. Instead of using the graduated jar, and thus mixing the gases, they may be prepared electrolytically with the same apparatus used for obtaining the mixed gases from water ; the bottle should, however, be a small one, and the electrodes must be of carbon. The electric current must be passed for a sufficient time to saturate the acid with chlorine. Instead of graduating the jar in cubic centimetres, fluid ounces may be used as the unit; then 4 oz. in volume of each gas should be employed.

As it is possible that the explosion which takes place when the spark is passed through the tube containing the mixture of gases might shatter the tube, the precaution of placing it in a

stink closet and shutting the door is advisable.   The eudio-
meter in which oxygen and hydrogen were exploded over
mercury cannot be employed, because mercury is rapidly
attacked by chlorine.   It is essential that the tube should be
dry before being filled with the gases ; to ensure this, it should
first be warmed in the hot-water oven, and the water vapour
sucked out.

CHAPTER IX.

69. Combination in Definite Proportion.—As the result of experimental examination of water and hydrochloric acid, the student is now in possession of a number of facts as to their composition. For convenience, these facts are presented in a tabular form in the following statement :—

Water, on being decomposed, yields hydrogen and oxygen in the proportion of 2 volumes of hydrogen to 1 volume of oxygen.

On recombination, 2 volumes of hydrogen and 1 volume of oxygen unite to form water, no gas of either kind being left over.

At temperatures at which water exists as a gas (steam), 2 volumes of hydrogen and 1 volume of oxygen unite to form 2 volumes of gaseous water.

By weight, 1 part of hydrogen combines with 7·98 parts (approximately 8) of oxygen to form 8·98 parts of water.

Hydrochloric acid, on being decomposed, yields hydrogen and chlorine in equal volumes, 1 to 1.

On recombination, 1 volume of hydrogen and 1 volume of chlorine unite to form 2 volumes of hydrochloric acid gas, leaving no excess of either hydrogen or chlorine.

It has been already stated that compounds are produced by the union of two or more elements in *definite proportions;* in the case of water and hydrochloric acid, proof is here afforded of the accuracy of the statement.

70. Actual Weight of Hydrogen, Oxygen, and Chlorine.—Before proceeding further with the study of the composition of bodies, a determination of the actual weight of hydrogen and the other elementary gases will be of much service. Directions for so doing follow, together with results obtained by students working in the manner directed.

Experiment 85.—Refer back, in the first place, to Exp. 2, in which is determined the weight of air. Fit up a vacuum pump, such as is there described, with a long tube, *ijkl* (Fig. 3), which will act as a mercury gauge. Prepare and clean the round-bottomed flask with indiarubber cock and glass stop-cock, *mno*, and attach to the pump. Exhaust by turning on a stream of water until no more air-bubbles are seen escaping with the waste stream from the pump. Turn off the water from the pump, and note how high the mercury stands in tube *ij*. Turn on the pump again for five minutes, and again note the height at which the mercury stands when the water is turned off. If necessary, repeat this operation until no improvement in vacuum is gained by further exhaustion. Shut the stop-cock *n* of the glass flask, remove same, and invert in a vessel of water recently well boiled, to expel air, and quickly cooled. Open the stop-cock gradually, and allow the flask to fill as far as it will with water. Shut off the stop-cock, remove the flask, turn it over, and withdraw the cork; pour off the water into a graduated litre jar, and measure amount; enter same in note-book. This gives the volume of air exhausted by the pump. Then completely fill the flask with water to level of bottom of cork, and again measure; this gives the total volume of the flask. In the author's laboratory the following results were obtained :—

	Cubic centimetres.
Capacity of flask to inside of cork . . .	1552
Volume of air exhausted by the pump . .	1465
Volume of residual air after exhaustion . .	87

In this case about 94·0 per cent. of the total air in the flask was exhausted; and, working with this particular pump till the maximum of vacuum was reached, 1465 c.c. of air were removed.

In the next place, arrange the following special apparatus (Fig. 36) for the preparation and collection of hydrogen from zinc and sulphuric acid. To a flask, *a*, of about 12 ozs. capacity, fit a good cork, through which bore two holes, and pass through the one an ordinary leading tube, *e*; through the other pass the stem, *d*, of a small glass "separator," *b*. This piece of apparatus consists simply of a pear-shaped or cylindrical body, *b*, stoppered at the top, and fitted at the bottom with a stop-cock, *c*, and delivery tube, *d*. Procure a stout cylindrical jar, *i*, about 6 inches in diameter and a foot high ; select a gas jar, *h*, open at the bottom and somewhat smaller than *i*, so as to easily slide up and down within it. Fit to the neck of *h* a good cork and leading tube, *g*, and connect to it, by means of indiarubber tubing, a glass stop-cock, *f*, in a piece of glass tubing. Arrange a stand, *j*, with a rising fork, *k*, so
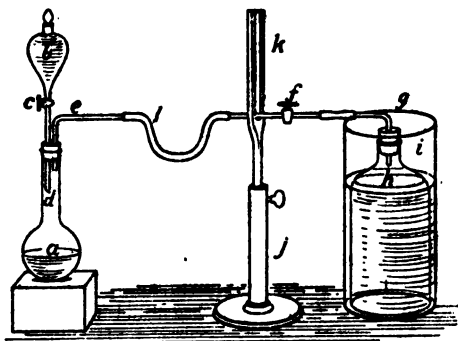
FIG. 36.—Collection of pure hydrogen in gas-holder.

adjusted that it may support *f* throughout its range of movement. With the further end of *f* disconnected and the stop-cock open, fill the jar *i* with water until it stands at a level both inside and outside of *h*, just below the lower end of the leading tube *g*. About half fill the flask *a* with water, introduce about an ounce of pure zinc in rods, and also put in a piece of stout platinum foil. (The object of this latter is to favour the evolution of hydrogen by setting up voltaic action between the platinum and the zinc, as has been already explained, p. 77.) Close the stop-cock *c*, and fill the separator *b* with concentrated

K

sulphuric acid.   Connect the leading tube *e* by indiarubber tubing to the stop-cock *f*, and open the latter.   The whole apparatus being in readiness, open the stop-cock *c*, and allow a few drops of sulphuric acid to fall into the flask, when hydrogen commences to be evolved.   Add a few drops more acid as required, so as to maintain a steadily evolved current of the gas. The hydrogen as produced passes over into the jar *h* and gradually fills it, the jar floating upwards as it becomes full. Let the evolved hydrogen completely fill the jar *h;* then disconnect the apparatus at the joint on *e*, and allow the whole of hydrogen in *h* to escape, and again connect up the apparatus and refill the jar *h*.   Then slip the indiarubber tubing off at *e*, at the same time pinching it at *l*, so as to close the passage ; then close the stop-cock *f*.   The object of once filling the jar and emptying it of gas is to sweep out of the whole apparatus the air which it originally contained.   At the close, *h* is full of practically pure hydrogen.   Meantime thoroughly clean and dry the flask fitted with stop-cock ;   connect it to the pump, and exhaust as thoroughly as possible.   Weigh most carefully, and enter the weight in the note-book.   Let the flask and weights remain on the balance, and again test after 15 minutes. There must be no increase in weight, as if so the flask is leaking and becomes heavier through ingress of air.   The flask must be handled as little as possible, and the fingers must be clean and *perfectly dry*.

Next attach the longer tube *p q* of a small wash-bottle charged with concentrated sulphuric acid, and, say, of 3 oz. capacity, to the end *l* of the indiarubber tube, as shown in Fig. 37.

To the exit tube *r* of this wash-bottle connect a ∪ tube *s t*, filled with fragments of pumice moistened with concentrated sulphuric acid.   Slip over the exit end of this ∪ tube a short piece of indiarubber tubing, closed at *u* with a spring pinch-cock.   Open the stop-cock *f*, and then slightly open the pinch-cock *u* so as to permit the gas in *h* to pass in a slow stream of bubbles through the wash-bottle and ∪ tube *s t*, driving out the air which they contain.   If necessary in order to cause the gas to pass, press slightly on the top of the jar *h*.   About one-quarter of the total gas in *h* may be thus used for freeing the wash-bottle and ∪ tube from air.   Next attach the exhausted and weighed flask *m n o* to the indiarubber tube beyond *u*.

Open the stop-cock *f*, and also the pinch-cock *u* (slip the tube from between the jaws of the pinch-cock into the round bow in its centre).   Next turn the stop-cock of the flask *n very cautiously*, so as to cause the gas to *bubble slowly* through the acid in the wash-bottle.   As the flask fills, the stream of bubbles
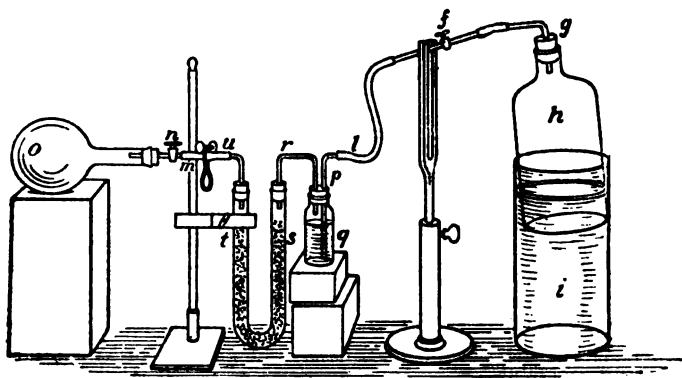
FIG. 37.—Filling exhausted flask with hydrogen.

becomes slower ; then *gradually* open the stop-cock *n*, until finally, with the stop-cock fully open, no more gas passes.   The flask is now full of hydrogen ; shut the stop-cock *n*, and also *f ;* disconnect the flask *m n o*, and again weigh.   Note the temperature of the air at the time, and also the height of the barometer in millimetres.

   The following data were thus obtained by one of the author's students :—

   Weight of flask and hydrogen .   .   . 235·61 grams.
      ,,   exhausted flask   .   . 235·49   ,,
      ,,   1465 c.c. of hydrogen   .   .   0·12   ,,
   Temperature at time of experiment   .   15·0° C.
   Height of barometer at time of experiment   770 mm.

   It is first necessary to determine what volume is occupied by the 1465 c.c. of gas when reduced to normal

temperature and pressure. This is easily calculated if the laws governing volume of gases, par. 21, be remembered—

$$\frac{1465 \times 273 \times 770}{288 \times 760} = 1407 \text{ c.c. at N.T.P.}$$

By experiment we have thus found 1407 c.c. of hydrogen at N.T.P. to weigh 0.12 gram ; from this it is easy to calculate the weight of 1 litre = 1000 c.c. :—

$$\frac{0.12 \times 1000}{1407} = 0.0853, \text{ weight of 1 litre of hydrogen at N.T.P.}$$

Proceed next to determine, in a similar manner, the weight of oxygen, which for the purpose should be prepared by heating potassium chlorate. The temperature at which the gas is evolved being somewhat high, a flask of difficultly fusible glass should be employed. Flasks specially suitable for purposes such as this are now made at Jena, and are known as "Jena flasks." Take a long-necked Jena flask of about 6 oz. capacity, and fit it up with an ordinary cork and single delivery tube. Introduce into the flask an ounce of potassium chlorate, and then insert in the neck of the flask a plug of cotton-wool, so as to come just below the cork. This must be tight enough not to drop down into the body of the flask, but must be loose enough to permit the passage of gas. (The object of this plug is to filter off any volatilized solid salts, which otherwise would be carried over with the gas.) Fix the flask in a retort-stand, and connect to the end *l* of the indiarubber tube of the gas-holder used for the experiment with hydrogen (after, of course, allowing all gas to escape). It is well to stand the retort-stand on a sheet of iron, in order to catch any melted chlorate in event of the flask breaking. Open the stop-cock *f,* and heat the chlorate gradually and carefully until the jar *h* is full. As before, momentarily disconnect and reject the first lot of gas ; reconnect and again fill the holder *h.* Disconnect the tube at *l,* and shut the stop-cock *f.* Meantime clean the flask *m n o,* allowing it to stand open for some minutes with the mouth upwards, so as to permit the whole of the hydrogen it previously contained to escape. Exhaust and weigh the flask ; then

connect up the gas-holder, wash-bottle, U tube, and exhausted flask precisely as before (Fig. 37), and, with the same precautions, allow the flask to fill with oxygen. Close the stopcock *n*, disconnect, and weigh.

The following data were thus obtained by one of the author's students :—

Weight of flask and oxygen . . . 237·515 grams.

,, exhausted flask . . . 235·500 ,,

,, 1465 c.c. of oxygen . . 2·015 ,,

Temperature at time of experiment . 15° C.

Height of barometer at time of experiment 770 mm.

Calculating as before, 1465 c.c. at 15° C. and 770 mm. are equal to 1407 c.c. at N.T.P. Then—

$$\frac{2·015 \times 1000}{1407} = 1·4321,$$ weight of 1 litre of oxygen at N.T.P.

Proceed next to determine, in a similar manner, the weight of chlorine. To prepare the gas, fit up a 32-oz. flask with the separator *b c d* (Fig. 36) instead of a thistle funnel. Pour in some hydrochloric acid, then the manganese dioxide ; cork up, and add more acid through the separator. Place the flask on a retort-stand, connect to the gas-holder, shake the flask so as to mix the acid and dioxide, and then apply a gentle heat. Fill the holder with chlorine, reject as before, and refill. Working in this way, the gas may be collected quite readily over cold water. Attach the sulphuric acid wash-bottle and U tube, and fill the weighed and exhausted flask with chlorine. Disconnect and weigh.

The following are a student's data thus obtained in the author's laboratory :—

Weight of flask and chlorine . . . 239·98 grams.

,, exhausted flask . . . 235·52 ,,

,, 1465 c.c. of chlorine . . 4·46 ,,

Temperature at time of experiment . 15° C.

Height of barometer at time of experiment 770 mm.

Calculating as before, the 1465 c.c. equal 1407 c.c. at N.T.P., and—

$$\frac{4\cdot46 \times 1000}{1407} = 3\cdot169, \text{ weight of 1 litre of chlorine at N.T.P.}$$

By our own experiments, we now have a knowledge of the approximate weights of hydrogen, oxygen, and chlorine. To determine these with perfect accuracy, many precautions must be taken, and far more delicate apparatus employed than is at the disposal of the elementary student. Below are given the weights obtained in the previously described experiments, and also the weights as determined under the most exact conditions, and accepted as correct by chemists :—

ABSOLUTE WEIGHT OF GASES IN GRAMS.

			Determinations by student.	Exact determinations.
Hydrogen, 1 litre at N.T.P. weighs			0·0853	0·0896
Oxygen,	1	,, ,,	1·4321	1·4300
Chlorine,	1	,, ,,	3·1690	3·1691

Remembering that hydrogen is the lightest substance known, we may next calculate the density of these gases in terms of hydrogen taken as unity. This is determined by dividing each of the above figures by the weight of hydrogen—

$$\text{Hydrogen, } \frac{0\cdot0896}{0\cdot0896} = 1\cdot0.$$

$$\text{Oxygen, } \frac{1\cdot4300}{0\cdot0896} = 15\cdot96.$$

$$\text{Chlorine, } \frac{3\cdot1691}{0\cdot0896} = 35\cdot37.$$

As water is composed of 2 volumes of hydrogen combined with 1 volume of oxygen, or, expressing hydrogen as unity, of 1 volume of hydrogen combined with a half-volume of oxygen, we know, from the experimentally determined densities, that in water—

1 volume = 1 part by weight of hydrogen is combined with

$$0·5 \text{ volume} = \frac{15·96}{2} = 7·98 \text{ parts by weight of oxygen,}$$

to form 8·98 parts by weight of water.

This is also confirmed by the direct determination of composition by weight in Exp. 64.

Further, as hydrochloric acid consists of 1 volume of hydrogen combined with 1 volume of chlorine, it follows from the densities that—

1 volume = I part by weight of hydrogen is combined with
   1 volume = 35·37 parts by weight of chlorine, to form
   36·37 parts by weight of hydrochloric acid.

The student is now able to appreciate more fully the law that **when elements combine they do so in absolutely definite proportions.**

71. Chemical Equivalents.—Before attempting to grasp the meaning of the term "chemical equivalent," the student will do well to make the following experiment, which has as its object the determination of the quantity of hydrogen evolved from sulphuric acid by a definite weight of zinc.

Experiment 86.—Procure a gas-tube *a b* (Fig. 38) of 250 c.c. capacity, graduated into 250 divisions. Prepare some dilute sulphuric acid, 1 part acid to 15 of water ; fill the tube with this ; cover with a ground-glass plate, excluding all air, and invert in a small trough or bowl, *c d*, also filled with the dilute acid. Carefully clean a piece of pure zinc rod, and weigh off accurately on the delicate balance a fragment weigh- ing between 0·4 and 0·5 grams ; make a note of the weight. The next step is to dissolve this zinc in the dilute acid, and measure the evolved gas. Pure zinc dissolves, however, some- what slowly, but, as the result of voltaic action, is attacked much more rapidly when *in contact* with platinum. Take, therefore, a small platinum capsule, *e*, or crucible lid, place the piece of zinc in it; and *very quickly* introduce it under the gas- jar, as shown in the figure. (In the absence of a platinum

capsule, one of porcelain may be used, in the bottom of which a piece of platinum foil is placed.)   Bubbles of hydrogen are evolved as the zinc gradually disappears. As soon as the action is over, let the apparatus stand until at the temperature of the room ; then read off exactly how many cubic centimetres of gas have been evolved, and the temperature and height of the barometer at the time. Calculate what volume of gas at N.T.P. has been evolved ; and then, knowing the weight of hydrogen, calculate what weight of zinc is necessary in order to displace 1 part by weight of hydrogen.
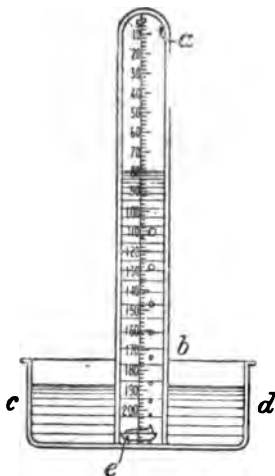
FIG. 38.—Measurement of hydrogen evolved by zinc.

Make another precisely similar experiment, except that magnesium is substituted for zinc, using, however, less magnesium, a very convenient quantity being about 0·2 gram. Fairly stout wire, or preferably even thin rod, should be employed.   It is also advisable to use more dilute acid, say about 1 in 30.   It is not necessary to use a platinum capsule, as the gas comes over very readily and quickly. Read off the quantity of gas, and calculate as before the weight of metal necessary in order to displace 1 part by weight of hydrogen.

If time permits, these experiments may be repeated with the use of hydrochloric acid solution instead of sulphuric acid. Dilute the acid to about 1 in 5 for the zinc, and half that strength for the magnesium. (In any case, it is well to make the magnesium experiment.)

Experiments made by one of the author's students gave the following results, sulphuric acid being employed :—

Weight of zinc taken	0·523 gram.
Volume of gas evolved	194 c.c.
Temperature.	12° C.
Height of barometer	766 mm.

Then—

$$\frac{194 \times 273 \times 766}{285 \times 760} = 187 \text{ c.c. of gas at N.T.P.}$$

$$\frac{187 \times 0.0896}{1000} = 0.01675 \text{ gram of hydrogen.}$$

$$\frac{1 \times 0.523}{0.01675} = 31.2, \text{ weight of zinc required to displace 1 part by weight of hydrogen.}$$

Weight of magnesium taken .	.	0.159 gram.
Volume of gas evolved	.	161 c.c.
Temperature . . .	.	12° C.
Height of barometer . .	.	766 mm.

$$\frac{161 \times 273 \times 766}{285 \times 760} = 155 \text{ c.c. of gas at N.T.P.}$$

$$\frac{155 \times 0.0896}{1000} = 0.0138 \text{ gram of hydrogen.}$$

$$\frac{1 \times 0.159}{0.0138} = 11.5, \text{ weight of magnesium required to displace 1 part by weight of hydrogen from sulphuric acid.}$$

Using magnesium and hydrochloric acid, the following results were obtained :—

Weight of magnesium taken .	.	0.177 gram.
Volume of gas evolved .	.	177 c.c.
Temperature . . .	.	12° C.
Height of barometer .	.	766 mm.

$$\frac{177 \times 273 \times 766}{285 \times 760} = 170 \text{ c.c. of gas at N.T.P.}$$

$$\frac{170 \times 0.0896}{1000} = 0.0152 \text{ gram of hydrogen.}$$

$$\frac{1 \times 0.177}{0.0152} = 11.6, \text{ weight of magnesium required to displace 1 part by weight of hydrogen from hydrochloric acid.}$$

In confirmation of the foregoing results, or as an alternative, in case the absolute weight of hydrogen has not been determined, the weight of hydrogen displaced from sulphuric acid by magnesium and zinc respectively may be estimated by direct weighing in the manner described in the following experiment.

Experiment 87.—Procure the apparatus illustrated in Fig. 39, and known as Schroedter's carbon dioxide apparatus. The apparatus consists of a very light flask, *a*, fitted with a stopper in the side, *b*. To the right, on the top, is shown a small reservoir, *d*, provided with a stopper and stop-cock, *c*, from which latter a bent tube, *e*, leads to the bottom of the flask. To the left is an exit tube, *ff*, enclosed within another tube, *g*, which in its turn is contained within the tube *h*. This latter is provided with a stopper, *i*, pierced with a small hole. In use, the apparatus is first wiped perfectly dry and clean throughout all its parts. The stop-cock *c* is closed, and the reservoir *d* is filled with dilute sulphuric acid, 1 to 3. The arrangement of tubes *f*, *g*, *h* is provided for the purpose of thoroughly drying the escaping gas, which finds its way up through *ff*, down between *ff* and *g*, then through some holes at the bottom of *g* leading into the outer space, and then up between *g* and *h*, and out through the stopper *i*. To make a determination, clean the apparatus, and by means of a funnel or small pipette fill the reservoir *d* as directed. Take out the stopper *i*, and with the aid of a small funnel carefully fill *h* to about two-fifths of its height with concentrated sulphuric acid. No acid must be spilled on the outside of the apparatus during either of these

FIG. 39.—Apparatus for determination of weight of evolved gases.

operations, and, if possible, the insides of the necks of the two reservoirs must not be wetted. Next replace the stopper *i*, and attach to it a small length of indiarubber tubing ; take out the stopper *b*, and suck *very gently* through the rubber tube ; the acid rises in *h* and falls in *g* until the latter is empty ; bubbles of air then pass up through *h* and escape through *i*. At this stage the tube *h* must be about four-fifths full of acid, but the quantity used must not be sufficient to cause any risk of particles of acid being carried over with the escaping gas through *i*. With an apparatus new to the student, it is well to first try it with rather less acid, and afterwards add a little more if the apparatus will take it. Introduce about 10 c.c. of water into *a* through the opening *b*. The apparatus being now ready for a determination, as a final precaution, take out each stopper, *b, g, i*, and see that they are dry; if not, wipe each on a piece of old duster, and with the same wipe also the insides of the necks of the various openings. Handle the apparatus as little as possible with the warm hand, and during these last cleanings remove the stopper at *b*.

Next weigh off accurately a piece of stout magnesium wire, between 0·3 and 0·4 gram in weight, and break it up into convenient lengths to go in the apparatus. Introduce the magnesium through the opening *b*, and allow the apparatus to stand two or three minutes, in order to get to the temperature of the air. Then introduce the stopper *b*, and weigh the whole apparatus as carefully as possible.

Lift the stopper of *d* so as to permit the passage of air, and slightly turn the stop-cock *c* so as to admit a few drops of acid into *a*. Give the apparatus a gentle rotary motion so as to mix the acid and water, holding it for this purpose by the reservoir. A gentle stream of hydrogen is evolved, and passes up through the tubes *f, g, h*, bubbling through the contained sulphuric acid. From time to time admit a little more acid from *d*, and so regulate the evolution of hydrogen as to cause it to bubble steadily, but not too rapidly, through *f, g, h ;* a convenient rate is about two bubbles per second. Continue this action until the whole of the magnesium has disappeared. Nothing can now have escaped from the apparatus but air and hydrogen, as any water vapour will have been arrested and absorbed by the concentrated acid in *f, g, h*. To remove the hydrogen which still remains in *a*, it is necessary to draw air

through the apparatus until the whole of the hydrogen is thus washed out. But as the air is usually moist, it is evident that thus drawing moist air into *a*, and drying the same as it made its exit through *f, g, h*, will tend to increase the weight of the whole apparatus by absorption of water vapour from the air. To obviate this, remove the stopper *g*, and introduce in its place a cork and leading-tube, which latter is connected to the exit tube of a small wash-bottle containing concentrated sulphuric acid. Slip a piece of indiarubber tubing over the perforated stopper *i*, and gently suck a current of air through the apparatus for about a minute. Disconnect the rubber tubing, replace the stopper *g*, and weigh the whole apparatus. Reconnect to the wash-bottle, and again draw dry air through the apparatus as before. Again disconnect and replace the stopper, and weigh once more. The weight is probably increased, as a result of replacing, by dry air, hydrogen contained in the apparatus. Continue to repeat this operation of drawing dry air through the apparatus and weighing until the weight is constant between two successive weighings. Finally deduct the last or constant weight from the original weight of the apparatus ; the difference is the weight of hydrogen displaced by the quantity of magnesium used for the experiment. From this calculate the weight of magnesium necessary in order to displace one part by weight of hydrogen. At the close, wash out the flask portion of the apparatus through *b*, and either pour off the concentrated sulphuric acid from *h*, or allow it to remain in case another estimation is to be at once made.

For the zinc determination, weigh off from 1 to 1·2 gram of pure rod zinc, and charge the reservoir *d* with sulphuric acid diluted with an equal volume of water. Charge *h*, as before, with concentrated sulphuric acid for drying purposes. Make sure that the flask portion *a* is clean and perfectly free from acid ; introduce into it 10 c.c. of water. Then add the weighed portion of zinc, and weigh the whole apparatus. The zinc, being in the rod form, offers but little surface to the acid, and so dissolves but slowly : half the total acid in *d* may be run in at once, and a slow and steady current of hydrogen will be evolved. As it slackens, the remainder (or as much as necessary) of the acid may be run in. The reaction being complete, allow the apparatus to cool, and aspirate (draw) *dry* air through it as before, until the weight is constant. Calculate

the weight of zinc necessary to displace 1 part by weight of hydrogen.

The following are details of two tests made in this manner :

Weight of magnesium used　　.　　.　　.　　0·350 gram.
　　,,　　　charged apparatus　　.　　.　　.　　54·553 grams.
　　,,　　　apparatus after evolution of hydro-
　　　　　　　　　　　　gen, 1st weighing　54·514　,,
　,,　　　　　,,　　　　,,　　　2nd　　,,　　.　54·521　,,
　,,　　　　　,,　　　　,,　　　3rd　　,,　　.　54·523　,,
　,,　　　　　,,　　　　,,　　　4th　　,,　　.　54·525　,,
　,·　　　　　,,　　　　,,　　　5th　　,,　　.　54·526　,,
　,,　　　　　,,　　　　　　　 6th　　,,　　.　54·526　,,

54·553 − 54·526 = 0·027 gram of hydrogen evolved.

$\dfrac{0·350}{0·027}$ = 12·9, weight of magnesium necessary to displace 1 part by weight of hydrogen.

Weight of zinc used　.　　.　　.　　.　　.　　1·435 grams.
　　,,　　　charged apparatus　　.　　.　　.　　58·345　,,
　　,,　　　apparatus after evolution of hydro-
　　　　　　　　　　　　gen, 1st weighing　58·286　,,
　,·　　　　　,,　　.　　,,　　　2nd　　,,　　.　58·288　,,
　,,　　　　　,·　　　··　　　3rd　　··　　.　58·302　,,
　,,　　　　　,,　　　·,　　　4th　　,,　　.　58·303　,,
　,,　　　　　,,　　　　,,　　　5th　　,,　　.　58·303　·,

58·345 − 58·303 = 0·042 gram of hydrogen evolved.

$\dfrac{1·435}{0·042}$ = 34·1, weight of zinc necessary to displace 1 part by weight of hydrogen.

These figures agree fairly well with those obtained by calculation of weight from observed volume. The results are summarized in the following table, in which are also given those accepted as accurate by chemists generally, as the result of the most careful determinations possible.

WEIGHT OF METAL NECESSARY TO DISPLACE 1 PART BY WEIGHT OF HYDROGEN.

	Calculated from volume.	Estimated by direct weighing.	Accurate determinations.
Magnesium	. 11·5a	. 12·9	. 11·97
„	. 11·6b		
Zinc	. 31·2	. 34·1	. 32·45

a, displaced from sulphuric acid; b, displaced from hydrochloric acid.

Carrying these investigations a step further, the student is reminded that in Exp. 14, he observed that certain metals are capable of displacing others from their compounds, the example given being that in which iron displaces copper. When such displacement occurs, the weights of displacing and displaced metals also bear a constant relation to each other. Let us further examine this relationship more particularly in the case of the metals magnesium and zinc, with which we have already been experimenting.

Experiment 88.—Weigh off 4 grams of pure crystallized silver nitrate, and dissolve it in 50 c.c. of distilled water. Place 25 c.c. of the solution in each of two small clean beakers.

Weigh off from 0·1 to 0·12 gram of magnesium, and place it in the one beaker.

Weigh off from 0·25 to 0·3 gram of zinc, and place it in the other.

The magnesium and zinc will immediately commence to dissolve, with the deposition of metallic silver in the form of a greyish powder or more or less crystalline incrustation. Stir from time to time with small glass rods, and break down the incrusting masses; continue this until the whole of the zinc and magnesium respectively has entirely disappeared. Fold some paper filters, and pour the contents of the beakers on to them. In each case carefully transfer the whole of the metallic silver to the filter without losing any particles. Wash out the beakers with hot water, and pour this also on to the filters.

Each filter should thus be washed four times, using about 50 c.c. of water on each occasion, and allowing it to run through completely before the next washing. Place the funnels containing the filters in a hot-water drying oven, and let them remain there until perfectly dry. *Note.*—In any such experiments as this, carefully mark each funnel and filter so as to know which is which throughout.

When the filters are dry, take a small porcelain crucible, dry it by gently warming over the Bunsen flame, the crucible being supported on what is known as a pipeclay triangle. When again cold, weigh the crucible. Spread a sheet of clean glazed paper on the table or bench, place the crucible on it, and pour the silver from one of the filters into it as completely as possible. Carefully unfold the filter, and, by rubbing its surface together, rub off as much as possible of the adherent silver, and put it in the crucible. If any particles of silver have been spilled, brush them also carefully off the glazed paper into the crucible. Next take the filter paper, fold it with the silver side inwards, and wrap up into a little cylindrical coil about three-quarters of an inch long and a quarter-inch in diameter. Take a piece of platinum wire some 12 inches long, and commence to wind this round the coil of paper, commencing at one end and finishing at the other. Hold the coil by the end of the platinum wire into the flame of a Bunsen until completely burned to a white or whitish-grey ash. Carefully shake this out of the platinum wire into the crucible. This ash consists mostly of adherent silver, that of the paper itself being so little as to be a negligeable quantity in an experiment of this kind, being, with good paper, less than 0·001 gram. Gently dry the contents of the crucible over the flame, allow to cool, and weigh. Transfer the silver to a bottle of silver residues, and clean and weigh the crucible for the next determination.

Weigh the amount of silver from the other paper in precisely the same manner.

In the next place, proceed to determine the weight of copper precipitated by zinc. Weigh out 3 grams of crystallised copper sulphate, and dissolve in 50 c.c. of water. Weigh off from 0·5 to 0·6 gram of zinc, and place it in the solution of copper sulphate. The zinc slowly dissolves and precipitates copper. When the zinc has disappeared, collect the copper on a filter, wash, dry, and weigh as directed for the silver.

The following results were obtained by one of the author's students :—

Weight of magnesium used . . 0·113 gram.
    „   crucible and silver . . 8·723 grams.
    „   crucible. . . . 7·727 „
    „   displaced silver . . 0·996 „

Knowing already that 11·97 parts by weight of magnesium displace 1 part by weight of hydrogen, let us see what weight of silver this same weight, 11·97, of magnesium displaces :—

$$\frac{0·996 \times 11·97}{0·113} = 105·5,$$ weight of silver displaced by 11·97 parts of magnesium.

Weight of zinc used . . . 0·320 gram.
    „   crucible and silver . . 8·761 grams.
    „   crucible . . . 7·727 „
    „   displaced silver . . 1·034 „

Then, as 32·45 parts by weight of zinc displace 1 part by weight of hydrogen—

$$\frac{1·034 \times 32·45}{0·320} = 104·7,$$ weight of silver displaced by 32·45 parts of zinc.

Taking next the copper displacement :—

Weight of zinc used . . . 0·589 gram.
    „   crucible and copper . 8·288 grams.
    „   crucible . . . 7·727 „
    „   deposited copper . . 0·561 „

Then—

$$\frac{0·561 \times 32·45}{0·589} = 31·3,$$ weight of copper displaced by 32·45 parts of zinc.

It would have been interesting to complete the series by determining the weight of copper displaced by magnesium :

this, however, is somewhat difficult, as the magnesium in part displaces copper and in part displaces hydrogen from the solution of copper sulphate, hence the experiment is somewhat complicated. But if, with proper precautions, the weight of magnesium employed in displacing copper only be determined, it is found that, as in the case of silver, so also in the case of copper, 11·97 of magnesium and 32·45 parts of zinc respectively displace the same weight (31·50) of copper from a solution.

It will be convenient at this stage to summarize the results of our whole series of experiments. In the following table the results thus obtained are indicated by heavy type, the figures introduced being those which are accepted by chemists as correct for each determination when made under conditions of absolute accuracy. For purposes of comparison and further illustration, there are also introduced the results of other determinations of a similar character, these latter being printed in ordinary type. Parts by weight are understood throughout.

1 part of hydrogen combines with 7·98 parts of oxygen to form water.

1 ,, ,, ,, 15·96 parts of oxygen to form hydrogen peroxide, or hydroxyl.

1 ,, ,, ,, **35·37 parts of chlorine to form hydrochloric acid.**

35·37 parts of chlorine displace 7·98 parts of oxygen from water, with the formation of hydrochloric acid.

32·45 ,, zinc ,, 1 part of hydrogen from sulphuric acid.

11·97 ,, magnesium ,, 1 part of hydrogen from sulphuric acid.

11·97 ,, ,, ,, 1 part of hydrogen from hydrochloric acid; and at the same time—

11·97 ,, ,, combine with 35·37 parts of chlorine to form magnesium chloride.

32·45 parts of zinc combine with 1 part of hydrogen from hydrochloric acid.

27·95   „   iron   „   1 part of hydrogen from hydrochloric acid.

27·95   „   „   :   31·50 parts of copper from copper chloride; and at the same time—

27·95   ,·   ,·   „   35·37 parts of chlorine.

31·50   „   copper   ,,   15·99 parts of sulphur.

7·98   „   oxygen   and   99·90 parts of mercury are obtained by the decomposition of mercury oxide.

11·97   „   magnesium displace   107·66 parts of silver from silver nitrate.

32·45   „   zinc   „   107·66 parts of silver from silver nitrate.

11·97   „   magnesium „   31·50 parts of copper from copper sulphate.

32·45   „   zinc   „   31·50 parts of copper from copper sulphate.

31·50   „   copper   „   99·90 parts of mercury from mercury chloride.

35·37   ,·   chlorine   „   79·75 parts of bromine from hydrobromic acid.

35·37   ·,   „   „   126·53 parts of iodine from hydriodic acid.

79·75   „   bromine   „   126·53 parts of iodine from hydriodic acid.

In the three compounds, hydrochloric, hydrobromic, and hydriodic acids, 1 part of hydrogen is combined respectively with 35·37 parts of chlorine, 79·75 parts of bromine, and 126·53 parts of iodine. From the statements just given, the following deductions may readily be made :—

(1) 1 part of hydrogen may combine with, or be displaced from, a compound by

{
7·98 parts of oxygen.
35·37   „   chlorine.
11·97   „   magnesium.
32·45   „   zinc.
27·95   „   iron.
79·75   „   bromine.
126·53   „   iodine.
}

(2) 7·98 parts of oxygen ⎫
    35·37   ,,   chlorine ⎬ May each replace the
    79·75   ,,   bromine ⎬ other in certain chemi-
    126·53   ,,   iodine ⎭ cal compounds.

(3) 99·90 parts of mercury ⎫
    107·66   ,,   silver ⎬ May replace each
    31·50   ,,   copper ⎬ other, or 1 part of
    27·95   ,,   iron ⎬ hydrogen, in cer-
    11·97   ,,   magnesium ⎬ tain compounds.
    32·45   ,,   zinc ⎭

The weights here given are said to be equivalent to each other in these various compounds. As hydrogen is here represented by 1, it is taken as the standard for comparison of the others, and accordingly, **the weight of an element which combines with, or by displacement expels from, a compound one part by weight of hydrogen, is termed its "chemical equivalent."** In passing, let it be carefully noted that the chemical equivalents are simply expressions of the results of actual experimental determinations ; they are in no way dependent on any chemical theory or hypothesis.

72. Atomic Theory.—The student is now in a position to appreciate and understand more fully the explanation of the atomic theory, which has already been given in Chapter III., and will do well, with the knowledge of experimental data which he now possesses, to again carefully read and study that explanation. The experiments described in this chapter will have demonstrated to him the fact already mentioned in Paragraph 35 on "Atoms and Molecules," "that the quantity of every element which enters into combination is either a certain definite and unchangeable weight, or a multiple of that weight." For example, zinc has been used to displace both hydrogen and silver from compounds, and 32·45 parts of zinc in each case displace respectively 1 and 107·66 of hydrogen and silver. Also 11·97 parts of magnesium displace the same weights

of hydrogen and silver as did the 32·45 parts of zinc. Looking through the table in Paragraph 71, he will see how the same number applies to the same element in a number of reactions of different character. It is an easy step from this to the explanation of the atomic theory given in the thirty-fifth paragraph. On referring to the Table of Elements and their combining or atomic weights, p. 46, it will be seen that these weights are either identical with or closely related to the chemical equivalents as determined by experiment. Thus the equivalents of hydrogen, chlorine, silver, bromine, and iodine are the same as their atomic weights, while the equivalents of oxygen, zinc, magnesium, copper, and mercury are just half the atomic weight. In fact, the atomic weight is either identical with the chemical equivalent, or some simple multiple of that number. A full explanation of the laws which govern the determination of the atomic weight cannot be given here, but one such at least may be explained. Oxygen has as its equivalent the number 7·98; why not, then, call the atomic weight of oxygen 7·98, and write the formula of water HO? The reason is obvious; hydrogen can be displaced from water in two distinct instalments, and therefore, according to the definition of an atom, there must be at least two atoms of hydrogen in water. Therefore, for this and other reasons, water is considered to consist of two atoms of hydrogen to one of oxygen; consequently 2 parts of hydrogen by weight are looked on as combining with 15·96 by weight of oxygen; and, as no less proportion of that element is ever displaced from a chemical compound, 15·96 is taken as the atomic or combining weight of oxygen. As a result of determinations of the chemical equivalents and certain other properties of elementary bodies, it is possible to assign to every element a number, which number or its multiple shall represent the proportionate quantity by weight of that element which enters into any chemical compound. These numbers are termed the "combining

or atomic weights" of the elements, and are deduced from results obtained on actual analysis.

73. Combination in Multiple Proportions.— The oxides of hydrogen, water and hydrogen peroxide, afford examples of two elements combining in more than one proportion. It will be observed that in the one compound exactly double the quantity of oxygen is combined with 1 of hydrogen as there is in the other. Taking other series of compounds into consideration, it is found throughout that a very simple relation exists between the proportions of each element found in the various compounds. In fact, **not only does chemical combination invariably occur in definite proportions, but also, when two elements happen to combine in more than one proportion, they unite in multiple proportions.** It may seem strange that this law was not discovered earlier in the history of chemistry than it was, but if the composition of bodies be expressed simply in percentages instead of being represented by formulæ, the fact is not so evident. To give an example, there are two compounds of carbon and oxygen which have respectively the following percentage compositions :—

	No. 1.	No. 2.
Carbon	42·857	27·273
Oxygen	57·143	72·727
	100·00	100·00

On the surface there is here no evidence of combination in multiple proportion ; 42 is no simple multiple of 27, neither is 72 of 57. But let us in each case see what weight of oxygen is combined with one part by weight of carbon : this is determined by dividing the weight of oxygen by that of carbon in each compound :—

$$\text{No. 1.} \quad \frac{57\cdot143}{42\cdot857} = 1\cdot33 \text{ of O to 1 of C.}$$

$$\text{No. 2.} \quad \frac{72\cdot727}{27\cdot273} = 2\cdot66 \text{ of O to 1 of C.}$$

When stated in this manner, it is at once seen that to the unit of carbon there is twice as much oxygen in the latter compound as in the former.

The reason, according to the atomic theory, why combination occurs in multiple proportions is, that when two elements combine, one atom of the first may combine with one, two, or three atoms of the second, but combination with the *fraction* of an atom is necessarily a contradiction.

74. Chemical Calculations.—It is of the highest importance to the student that he should be able to make the various calculations necessary in analytic and other chemical work. It is now seen that the law of definite proportions underlies the whole basis of chemistry; an explanation of the methods of chemical calculation naturally follows.

75. Formula from Percentage Composition.— In the case of a new body, the first step in ascertaining its composition is to make an analysis, the results of which are almost always expressed in percentages. Suppose that an analysis of potassium chlorate has been made with the following results, and that its formula is required :—

Oxygen	.	.	.	.	39·18
Chlorine	.	.	.	.	28·97
Potassium	.	.	.	.	31·83
					99·98

A moment's consideration will show that we must first determine the proportionate number of atoms of each element present. Thus we have 39·18 parts by weight of oxygen : we know that the relative weight of the oxygen atom is 15·96 (or, for simplicity in calculation where extreme accuracy is not required, 16). Then, if we divide 39·18 by 16, we shall get a number proportionate to the number of atoms present. Dividing each number by the atomic weight of the element, we have—

$$\frac{39\cdot18}{16} = 2\cdot448 \text{ of oxygen.}$$

$$\frac{28\cdot97}{35\cdot5} = 0.816 \text{ of chlorine.}$$

$$\frac{31\cdot83}{39} = 0.816 \text{ of potassium.}$$

These numbers, $2\cdot448$, 0.816, and 0.816 are in the ratio of the number of atoms of each element present in the compound. The next step in the calculation is to find the smallest series of whole numbers which have the same ratio: dividing each of the numbers above by the lowest, we have—

$$\frac{2\cdot448}{0\cdot816} = 3 \text{ of O.} \quad \frac{0\cdot816}{0\cdot816} = 1 \text{ of Cl.} \quad \frac{0\cdot816}{0\cdot816} = 1 \text{ of K.}$$

The formula is therefore considered to be $KClO_3$. In assigning a formula to a compound, however, other considerations must not be overlooked; because the percentage composition will be the same whether we look on $KClO_3$ or $K_2Cl_2O_6$ as the formula. The above reasoning is conveniently summed up in the following rule for determining the formula from the percentage composition.

Rule.—Divide the percentage of each element by its atomic weight; divide each of the numbers thus obtained by the lowest one of the series; the quotients are generally whole numbers, or practically so. These represent the number of atoms of each element present in the molecule. In some cases the result of such division is that one quotient contains $0\cdot5$, *i.e.* one atom of one element to a proportion of $1\cdot5$ or $2\cdot5$, etc., of another; the number of atoms in the molecule is then obtained by doubling every number, making 2 of one to 3 or 5 of the other.

The student is not expected at this stage to determine whether the formula is really $KClO_3$ or $K_2Cl_2O_6$. By the above method the simplest formula of any compound is

obtained; other considerations must determine whether the formula is or is not a multiple of this. As a matter of fact, potassium chlorate, which has been taken as a convenient instance, is considered to be represented by $KClO_3$.

76. Percentage Composition from Formula.—At times it is convenient to perform the reverse operation to that described, and, knowing the formula of a body, calculate its percentage composition. The formula of a compound gives the number of atoms of each constituent; those atoms each being of a definite weight, we are enabled to state the proportion by weight of each element in a compound. Thus the formula of potassium chlorate is $KClO_3$; assigning to each of these their atomic weight, we have—

$$K \quad Cl \quad O_3.$$
$$39 + 35\cdot5 + (16 \times 3 =) 48 = 122\cdot5$$

that is, the molecule weighs $122\cdot5$, this being the sum of the weight of the constituent atoms. As any weight taken of this salt must consist of a whole though indefinite number of molecules, the proportion by weight of each element present is the same as that in the individual molecule. From the molecular weight of a compound its percentage composition, or weight of each constituent in 100 parts, is easily found by a calculation in proportion. Thus, in the case of potassium chlorate, $122\cdot5$ contain 48 of oxygen; what quantity will 100 contain?

As $122\cdot5 : 100 :: 48 \quad : 39\cdot18$ per cent. of oxygen.
„ $122\cdot5 : 100 :: 35\cdot5 : 28\cdot97$ „   chlorine.
„ $122\cdot5 : 100 :: 39 \quad : 31\cdot83$ „   potassium.

$$\underline{\quad\quad 99\cdot98}$$

Precisely the same method applies to any and every other compound.

77. Chemical Equation from Determination of Quantities.—The object of chemical equations is to

express symbolically the nature of a chemical change and of the quantities of the elements and compounds concerned therein. The student cannot at this stage make any very elaborate quantitative determinations of chemical changes, but there is one which he can well perform as an example of such determinations. He has already been informed as to the percentage composition of potassium chlorate, and has ·calculated its formula. Further, he knows that it evolves oxygen when heated : let us see how far he can go toward formulating the equation by which this change is represented.

Experiment 89.—Take a test‑tube made of combustion tubing 6 inches long and half an inch internal diameter ; fit to it a cork and leading tube about 2 inches long. Cut a piece about 2 inches in length from a glass tube about half an inch diameter ; fit a cork to each end ; insert the leading tube from the test-tube into one cork ; push in through the other end a loosely fitting plug of cotton‑wool, and through the cork pass a small piece of glass tubing. See that the joints are perfectly air-tight by sucking at the end leading tube and closing the tube with the tongue ; the comparative vacuum thus produced should not sensibly diminish during a few seconds. Dry the whole apparatus thoroughly by wiping with a dry and clean duster ; next weigh it. Before beginning to fit these parts together, a small quantity of potassium chlorate should be powdered and placed in the hot-water oven to dry. Having noted the weight of the apparatus, take the test-tube and scoop into it three grams or thereabout of the dry potassium chlorate ; give the tube a tap, so as to get all the salt at the bottom ; wipe out any particles adhering to the side of the tube with a small brush or the corner of the duster ; again weigh, and note the weight. Connect the leading tube ·by indiarubber tubing to a glass tube placed in the pneumatic trough. Fix the test-tube in the retort-stand, so that it is at an angle of 45°. Procure a tall graduated litre jar (a test-mixer), fill with water, and invert in the pneumatic trough to receive the gas. Fig. 40 shows the whole apparatus arranged for the evolution of oxygen. Warm the tube very gradually with the Bunsen ; the salt melts and

readily gives off oxygen. After a time, however, it becomes somewhat pasty, and the gas comes off less readily. At this point place the flame a little above the salt and heat carefully, working down toward the bottom. Toward the end heat the tube as strongly as possible with the Bunsen; turn it round, so that the whole of the salt is acted on ; when no more gas is evolved, disconnect the indiarubber and allow the apparatus to cool. The principal chances of failure are that the heat may so soften the glass that the gas may blow a hole through, and that

Fig. 40.—Determination of volume of gas evolved by potassium chlorate.

at the moment when the pastiness is produced the salt may bubble up into the higher part of the tube, and into the leading tube. This may be prevented by careful watching, using a tube of not less diameter than that given, and getting the tube hot just above the salt ; any which bubbles up is thus liquefied at the high temperature, and again runs back to the bottom. The little tube containing cotton-wool is fixed to retain any potassium chloride carried over mechanically with the gas. Remember that the plug must not be too tight, and that it must be at the end furthest from the generating tube.

When cold, weigh the tube and potassium chloride, and find what weight remains. Observe the volume of oxygen in the measuring jar when it is depressed until the level of the water inside corresponds with that in the trough. With a thermometer, take the temperature of the water, and calculate what volume the oxygen would be at 0° C. Then find by calculation

its weight. One litre of oxygen at N.T.P. weighs 1·4336 grams.

The following are results obtained in this experiment by a student working in the author's laboratory :—

Weight of apparatus and KClO₃ . . 43·68 grams.
    ,,   apparatus   . . . . 40·68 ,,
    ,,   KClO₃ .   . . . . 3·00 ,,
Weight of apparatus and residual salt = 42·62 ,,
    ,,   apparatus   . . . . 40·68 ,,
    ,,   residual salt . . . . 1·94 ,,

Volume of oxygen collected at 20° C. = 900 c.c. Reduced to standard temperature, correction for pressure being neglected—

$$\frac{900 \times 273}{293} = 838 \text{ c.c. at } 0° \text{ C.}$$

1000 c.c. of oxygen weigh 1·4336 gram.
As 1000 : 838 :: 1·4336 : 1·2013 gram of oxygen.

From the weight of potassium chlorate taken and of the products of the application of heat, it is easy to convert the results into percentages by a simple calculation in proportion—

As 3·00 : 100 :: 1·94 : 63·7 per cent. of residual salt.
As 3·00 : 100 :: 1·20 : 40·0 per cent. of oxygen.

Comparing these figures with the known percentage composition of potassium chlorate, we have—

				Percentage composition.	Found.
Potassium	.	.	.	31·83 ⎫ 60·80	63·7
Chlorine	.	.	.	28·97 ⎭	
Oxygen	.	.	.	39·18	40·0
				99·98	103·7

The figures agree comparatively nearly with those which

would result from the separation of the chlorate into free oxygen, and a residual compound of the potassium and chlorine. Let us next determine how nearly they correspond with the atomic and molecular weights of potassium chlorate and its constituent elements. We already know that potassium chlorate is represented by—

$$\text{K} \quad \text{Cl} \quad \text{O}_3.$$
$$39 + 35\cdot5 + (16 \times 3 =) 48 = 122\cdot5.$$
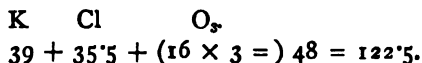
Then, by calculation in proportion—

As $3\cdot00$: $122\cdot5$ :: $1\cdot94$: $79\cdot21$, weight of residual salt yielded by molecular weight of potassium chlorate.

As $3\cdot00$: $122\cdot5$ :: $1\cdot20$: $47\cdot86$, weight of oxygen yielded by molecular weight of potassium chlorate.

Again comparing the figures resulting from the experiment with those representing the molecular weight of potassium chlorate we have—

				Molecular weight.	Found.
Potassium	.	.	.	$39\cdot0$ ⎫	
Chlorine	.	.	.	$35\cdot5$ ⎬ $74\cdot5$	$79\cdot21$
Oxygen	.	.	.	$48\cdot0$	$47\cdot86$
				$122\cdot5$	$127\cdot07$

These figures agree very closely with those which would result from splitting the molecule of potassium chlorate into free oxygen and a residual compound of potassium and chlorine (potassium chloride). The only other arrangement would be one in which a portion of the oxygen remained behind; but even if one atom did so, the residual salt would have to weigh $39 + 35\cdot5 + 16 = 90\cdot5$, while the evolved oxygen would only weigh 32. These figures would be altogether out of agreement with those obtained in the experiment, and therefore our results prove the decomposition into potassium chloride and free oxygen, which we accordingly represent by the equation—

$$KClO_3 \quad = \quad KCl \quad + \quad 3O.$$

	Potassium chlorate.	Potassium chloride.	Oxygen.
	$39+35\cdot5+48$	$39+35\cdot5$	3×16
Theoretical weight	$122\cdot5$	$74\cdot5$	$48\cdot0$
Found		$79\cdot21$	$47\cdot86$

By processes similar in principle to these the equations representing chemical changes are deduced.

In the particular experiment described the potassium chloride is over-estimated, through some of the chlorate probably remaining unreduced to chloride. The oxygen is so through the air in the test-tube expanding and being thus driven over. With care, however, results may be obtained which prove the general truth of the fact that the equation represents the weights of the various participating bodies; the error of experiment, even with a young student, should come within 4 or at most 5 per cent.

As further proof that the potassium chlorate is changed into another chemical compound by the action of heat, make the following experiment:—

Experiment 90.—In a clean test-tube dissolve the residuum of potassium chloride from the last experiment in a little distilled water. Add a few drops of a solution of silver nitrate, a curdy white precipitate is formed. In another clean test-tube dissolve a crystal of potassium chlorate, and again add silver nitrate solution; there is no precipitate. These tests show that the residual salt is a different chemical compound to the original potassium chlorate.

78. Calculation of Quantities from Chemical Equations.—Remembering the fact already demonstrated by an illustration, that chemical equations are simply symbolic representations of chemical changes, and, further, of the quantities of the participating bodies, it is a very simple matter to calculate the quantities of bodies engaged in any chemical change, if the equation representing that change is known. For example, refer back to the potassium chlorate experiment just made. We have taken 3·0 grams

of potassium chlorate; let us determine what, according to the equation, are the respective weights of oxygen to be driven off, and of potassium chloride to remain. From the equation as given in the last paragraph, we know that 122·5 parts by weight of potassium chloride yield respectively 48 parts by weight of oxygen, and 74·5 of potassium chloride. It is, then, simply a matter of simple proportion to calculate the quantities obtained from 3·0 grams :—

As 122·5 : 3·0 :: 48·0 : 1·175 grams of oxygen yielded.
As 122·5 : 3·0 :: 74·5 : 1·824   „   potassium   chloride
                                             remaining.

As another example of calculation of quantities, the following is given: Air contains 23 per cent. of its weight of oxygen: how many grams of phosphorus are needed to burn out the whole of the oxygen in 100 grams of air when the highest oxide of phosphorus is formed?

In dealing with all such problems, the first thing to do is to carefully consider what is the nature of the chemical change. The student already knows that phosphorus burns in air, and still more brightly in oxygen. He will find later on that air is a mixture of oxygen with certain inert gases, of which nitrogen is the chief. The reaction, therefore, is simply one of phosphorus burning to the pentoxide in the oxygen which the air contains. The next step is to remember the equation, which in this case is—

$$2P \quad + \quad 5O \quad = \quad P_2O_5.$$
$$31 \times 1 = 62 \quad 16 \times 5 = 80 \quad 62 + 80 = 142.$$
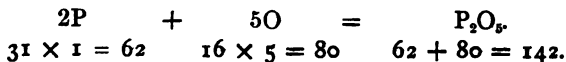
By the equation under which we have placed the atomic and molecular weights, in order to burn out 80 of oxygen, 62 of phosphorus will be required : then by the question there are 23 grams of oxygen present in 100 grams of air, and consequently—

As 80 : 23 :: 62 : 17·8 grams of phosphorus required to burn out 23 grams of oxygen in 100 grams of air.

To solve any such problem, it is necessary to know, first of all, what the exact nature of the chemical change is: *this is essential.* The change should then be expressed by an equation, which should be carefully checked to see that both sides balance. Having got thus far, the equation and a table of atomic weights give all the data required for calculations of quantities. These principles being understood, all these calculations resolve themselves into simple arithmetical problems.

79. Elementary Molecules and Nascent Condition.—The student already knows that the term "atom" is applied to the smallest particle of an element entering into or leaving a chemical compound; thus, when hydrochloric acid is decomposed, we say that an atom of each element is liberated. He is also aware that the atoms of elements, when in the free state, are not supposed to remain single, but in most cases unite together to form molecules of the element; thus two atoms of hydrogen unite to form a molecule of hydrogen. This union is attended with loss of the chemical activity of the element. It has been stated that *nascent* oxygen, liberated by chlorine, is a powerful bleaching agent, while free oxygen is not so. Also nascent hydrogen acts more powerfully as a reducing agent than does the same element when in its normal free state. This has already received partial explanation; the theory being that at the moment of liberation the oxygen exists as *atoms*, and these attack the colouring matter; failing anything else with which to unite, they unite with each other and form molecules. The activity of the oxygen molecule is less than the sum of that of the two atoms by the amount of energy with which they are held together. One striking experiment may be mentioned in which the affinity of oxygen atoms for each other is greater than that for the bodies with which they are combined :—

Experiment 91.—To a few drops of solution of nitrate of silver add, in a test-tube, an excess of sodium hydrate solution ;

a brown precipitate of oxide of silver is formed, which rapidly falls to the bottom. Wash two or three times by decantation ; pour on it some hydrogen peroxide (hydroxyl), and close the tube loosely with the thumb ; rapid effervescence ensues. When the action is over, test the gas in the tube for oxygen by a glowing splinter.

The following equation shows the chemical change which has occurred :—

$$\underset{\text{Hydroxyl.}}{H_2O_2} + \underset{\text{Silver oxide.}}{Ag_2O} = \underset{\text{Oxygen.}}{O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Silver.}}{2Ag.}$$
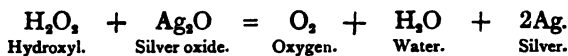
The affinity between the oxygen and silver is but small; so also is that between the water and second atom of oxygen which has changed it into hydroxyl. The attraction of the oxygen atoms for each other is sufficient to overcome these, and accordingly that element is liberated in the free state. Considerations of this kind have led the chemist to the conclusion that the atoms of elements combine together to form molecules.

80. Avogadro's Law.—The fact that all gases, whether elementary or compound, expand and contract at the same rate when subjected to variations of temperature and pressure has an important bearing on their probable molecular constitution. Their similarity in this respect has led to the assumption, expressed in the " Law of Avogadro "—" **Under similar conditions of temperature and pressure equal volumes of all gases contain the same number of molecules.**" From this it follows that at the same temperature, and under the same pressure, the volume of any gaseous molecule is the same, whatever may be the nature and composition of the gas.

81. Constitution of Molecules. — The relative weights of equal volumes of hydrogen and hydrochloric acid are 1 and 18·18. These, according to Avogadro, are the relative weights also of the molecules. By experiment we know hydrochloric acid contains half its volume of hydrogen ; it

must therefore contain half as much hydrogen as is contained by element as an equal volume of free hydrogen. The molecule of hydrogen then contains double as much hydrogen as is contained by a molecule of hydrochloric acid, which occupies the same volume. As we assume that the hydrochloric acid molecule contains at least one atom of hydrogen, the molecule of hydrogen must necessarily be composed of at least two atoms. The fact that two atoms of hydrogen are present in water was proved by its being removed in two successive portions; as the hydrogen of hydrochloric acid cannot be thus removed, this is strong evidence in favour of its containing *only* one atom; and as the quantity of hydrogen in the hydrogen molecule is double that in hydrochloric acid, it must be composed of two atoms, and no more than two. As the molecule of hydrogen consists of two atoms, its weight must be taken as 2, and that of the molecule of hydrochloric acid as 36·37.

82. **Combination by Volume.**—The student has seen that two volumes of hydrogen combine with one of oxygen to form two volumes of water-gas. If Avogadro's law be correct, this necessarily follows, because the molecule of steam occupies the same space as a molecule of hydrogen; and a still further condensation occurs in the production of more complex molecules. In the following equations the molecule is represented by two squares, indicating that the volume is double that of an atom :—

$$\boxed{H_2} + \boxed{Cl_2} \qquad\qquad = \boxed{HCl} + \boxed{HCl}$$

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} \qquad = \boxed{H_2O} + \boxed{H_2O}$$

$$\boxed{H_2} + \boxed{H_2} + \boxed{H_2} + \boxed{N_2} = \boxed{NH_3} + \boxed{NH_3}$$
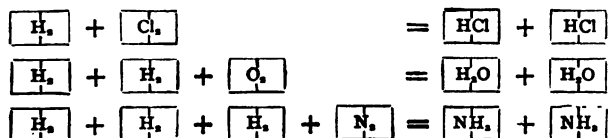
The first two reactions are already familiar to the student; the last represents the composition of ammonia gas; three volumes of hydrogen and one of nitrogen produce

M

only two volumes of gaseous ammonia (NH_3), and, consequently, on Avogadro's law, three molecules of hydrogen and one of nitrogen combine to produce two molecules of gaseous ammonia. The gaseous volume of elements in a compound is not only definite, but the volume of each element present is represented by a whole number.

The comparative volumes of gases taking part in any chemical change is, therefore, an important factor in the determination of the molecular equation, because, on application of Avogadro's law, it at once affords a means of deciding how many molecules of any particular gas are concerned. Conversely, the comparative volume of gases taking part in any chemical change may always be learned from the molecular equation by remembering that each molecule of a gas represents a unit of volume of that body. The error must not be made of writing an equation partly molecular and partly atomic.

83. Density and Molecular Weight of Gases.—

The density of a gas has already been defined as the weight of any volume compared with that of the same volume of hydrogen, measured at the same temperature and pressure and taken as unity. (These conditions are always understood in speaking of the comparative weights of gases.) As the molecule of hydrogen contains two atoms, its molecular weight, expressed in terms of atomic weight, is consequently 2. The molecular weight of any gas is the weight of that volume which occupies the same space as do two parts by weight of hydrogen. Conversely, as the molecular weight is the sum of the weights of the constituent atoms, the density of a gas may be determined from its formula. As the molecule of hydrogen weighs 2, the density of any gas, whether elementary or compound, is identical with the half of its molecular weight. For example, the molecule of steam weighs 18, and occupies the same space as the molecule of hydrogen, which weighs 2 ;

the quantity of steam occupying the same space as 1 volume of hydrogen must weigh $\frac{18}{2} = 9$.

84. Absolute Weight of Hydrogen.—Hydrogen being taken as the unit of density, its absolute weight is of great importance, and, therefore, an example of such determination has been set to the student. As a result of most careful weighing, it has been found that **1 litre of hydrogen at the normal temperature and pressure weighs 0·0896 gram, or 11·2 litres weigh 1 gram.** This figure 0·0896 gram is one which it is absolutely necessary that the student should remember : that the exact weight of 1 litre of hydrogen at 0° C. and 760 mm. pressure is 0·0896 gram, must therefore be thoroughly imprinted on the student's mind. Knowing this, there is no difficulty in calculating the weight of any other gas whose composition is known. **The weight in grams of a litre of any gas is its density × 0·0896. Further, the weight in grams of 11·2 litres of any gas is identical with the number representing its density.** The density of oxygen being 16, the weight of 1 litre at N.T.P. = 0·0896 × 16 = 1·4336 gram. The weight of a compound gas is found with equal readiness. The density of hydrochloric acid is 18·18 ; therefore the weight of a litre = 0·0896 × 18·18 = 1·6289 gram, or 11·2 litres weigh 18·18 grams.

This amount 0·0896 is of such frequent occurrence in chemical calculations that it has been proposed to give it a distinct name " Crith : " the weight of a litre of any other gas is then expressed as so many criths.

Summary.

That elements combine in definite proportions is proved by the experiments already made on the composition of water and hydrochloric acid. This is further elucidated by determinations of the actual weights of hydrogen, oxygen, and chlorine. That certain weights of hydrogen, magnesium, zinc, and other elements

are chemically equivalent to each other is proved by experiments in which proportions both by volume and by weight are determined. From this we come to the meaning of the term "chemical equivalent," and can see the step from such equivalents to "atomic weights," which are assigned to every element. Dalton explained this fact of there being a unit weight of combination and displacement belonging to each element by assuming that combination occurs between atoms of definite weights for each element. This also explains combination in multiple proportions. The formula of an element can be deduced from the percentage composition of a body as determined by analysis; conversely, knowing the formula, one can calculate the percentage composition. Having by analysis determined the quantities of elements and compounds concerned in any chemical reaction, the chemical equation may be formulated from such data; conversely, an equation gives the weight of each element and compound participating in a chemical reaction. From these may be reckoned the weight of any one body necessary for the production of a certain quantity of another; as, for instance, the quantity of potassium chlorate necessary to produce a certain weight of oxygen, or the weight of oxygen that may be obtained from a certain weight of potassium chlorate. Atoms of elements in the free state unite to form molecules. The molecules possess less energy than the atoms; therefore a gas when nascent is more active. The affinity between atoms of the same element is in some cases sufficiently great to cause the decomposition of unstable compounds. Molecules all occupy the same volume; the molecule of hydrogen contains two atoms. Even molecules containing a large number of atoms occupy the same space as a molecule of hydrogen; hence the union of hydrogen and oxygen to form water is accompanied by condensation. The density of all gases, both elementary and compound, is half the molecular weight. The weight of 1 litre of hydrogen at N.T.P. = 0·0896 gram; this number × density = the weight of 1 litre of any other gas.

OBJECT DEMONSTRATION.

Observe, in filling a flask with chlorine in order to weigh same, that from the very first moment the gas is perceptible it fills the whole of the flask equally.

LABORATORY DIRECTIONS.

Several of the experiments mentioned in this chapter are of a very delicate character, and require extreme care in order to get satisfactory results. They should, in the first place, be watched most carefully when performed on the lecture table, and then the very minute directions given with each experiment must be carefully followed.

85. Names of Metals.—The names given to the elements are, as a rule, in no way connected with their properties; the only attempt at system is that the termination *um* is reserved to the metals. Selenium and tellurium, however, are exceptions, as, when discovered, they were supposed to be metallic elements. It has been proposed to change the names to selenion and tellurion; this has not, however, met with general acceptance.

86. Binary Compounds.—Bodies which contain only two elements are called *binary compounds*. Their names are fixed by rule; but in the case of the more well-known compounds, the old or "trivial" names are almost always used; no one would think, for example, of calling water hydrogen monoxide. The name of a body should, as far as possible, indicate its composition; this end is attained by making the name of a binary compound consist of derivatives of the names of the two elements. There are unfortunately several modifications of each name, different chemists using different methods of nomenclature; the student must make himself familiar with the whole, as, in the course of reading, he is sure to meet with the same body under names different from one another. Very little practice is, however, sufficient to overcome this difficulty.

The most frequently occurring binary compounds are those composed of a metal and non-metal; the name of the metal is first written, and, one or more syllables being

removed, the termination *ide* is added to the name of the non-metal. The compound of copper and oxygen is thus called *copper oxide*, that of copper and sulphur, *copper sulphide*, and so on for other compounds. These names are sometimes written *oxide of copper* and *sulphide of copper* respectively. Another plan consists of changing the Latin name of the metal into an adjective by substituting *ic* for its last syllable; the above names thus become *cupric oxide* and *sulphide*.

We frequently find that more than one compound of the same elements is known; it then becomes necessary to use names which shall discriminate the one from the other. Oxygen and copper combine in two different proportions, represented by the formulæ CuO and Cu_2O; the name oxide is common to both, but the second is called cupr*ous* oxide. The termination *ous* is applied to the compound containing the lower proportion of oxygen or other non-metallic element. Where there are two or more atoms of the metalloid present in a compound, the distinction is marked by the use of a prefix to the second name, indicating the number. The two oxides of barium, BaO and BaO_2, are thus known respectively as barium monoxide and dioxide. Occasionally the prefixes *proto* and *per* are attached to the second name; *proto* to the compound in which the lower proportion of the non-metallic element occurs, *per* to that containing the higher; barium monoxide and dioxide become barium protoxide and peroxide. There is one series of oxides in which there are two atoms of the metal to three of oxygen, as Fe_2O_3: these are sometimes termed sesquioxides: the name is, however, dying out. Where there are several binary compounds of the same elements, or where the molecule is a complex one, the number of atoms of each element is indicated by a prefix thus, triferric tetroxide, Fe_3O_4. In binary compounds among the non-metals the termination *ide* is usually given in preference to oxygen, chlorine, and sulphur; thus we

have carbon oxides and sulphides, phosphorus chlorides, and chlorine oxides.

87. Ternary and Higher Compounds.—The name " ternary " is applied to those compounds containing three elements. Among the compounds higher than the binary series are those formed by the union of water with oxides, thus forming acids, and hydrates (hydroxides), and derivatives of these bodies.

In experimenting with oxygen the student will have observed that certain oxides dissolved in water turn litmus solution red, while others restore to the reddened solution its blue colour. This reaction serves to divide the various oxides into two important classes, to which attention must now be directed.

88. Acids.—The name acid is a familiar one, because it is continually applied in everyday parlance to anything which is sour. A number of bodies possess this distinction in common ; to the chemist the sourness of an acid is but an accidental property, as, according to his definition of these bodies, substances are included as acids that are not sour to the taste. **An acid may be defined as a body containing hydrogen, which hydrogen may be replaced by a metal (or group of elements equivalent to a metal) when presented to it in the form of an oxide or hydrate (hydroxide).** As a class, the acids are sour ; they are also active chemical agents. Most acids are characterized by the property of changing the colour of a solution of litmus, a naturally blue body, to a red tint. This, as the student has just been reminded, is one of the properties of the solution of certain oxides in water. In these instances chemical union occurs between the oxide and water, resulting in the production of an acid as a distinct chemical compound ; thus the addition of water to sulphur trioxide produces sulphuric acid :—

$$SO_3 \quad + \quad H_2O \quad = \quad H_2SO_4.$$
Sulphur trioxide.   Water.   Sulphuric acid.

Oxygen is a constituent of most acids, the members of this group being distinguished as "oxy-acids." The oxides which by union with water form acids are termed anhydrides, or anhydrous acids. They are in most cases non-metallic oxides, but sometimes consist of metals combined with a comparatively large number of atoms of oxygen. There are a few acids in which oxygen is absent : these are termed "hydr-acids :" hydrochloric acid, HCl, is an example of this class. According to the definition given (which is accepted by the great majority of chemists), hydrogen is an essential constituent of all acids. It should, however, be mentioned that some chemists apply the term "acid" to what are here termed anhydrides; consequently CO_2 (carbon dioxide, or carbonic anhydride) is sometimes described as carbonic acid gas. This name is now, however, being replaced by that more in accordance with the theories of modern chemical science.

89. Bases and Alkalies.—The oxides which, when dissolved in water, restore the blue colour to reddened litmus are called alkalies : they form a subdivision of a larger class of oxides, the whole of which combine readily with acids, and are known as bases.

A base is a compound, usually an oxide, or hydrate, of a metal (or group of elements equivalent to a metal), which metal (or group of elements) is capable of replacing the hydrogen of an acid when the two are placed in contact. The greater number of metallic oxides are bases. Bases, as well as acids, differ considerably in their chemical activity. As already mentioned, certain bases which dissolve in water are termed alkalies.

An alkali is a base of a specially active character, soluble in water, to which it imparts a soapy taste and touch. Alkalies restore the blue colour to reddened litmus. The principal alkalies are sodium hydrate, NaHO, and potassium hydrate, KHO. A solution of ammonia gas in water is also alkaline, and is often termed ammonium hydrate.

Paper tinted yellow with turmeric is also used as a test for alkalies, which give the paper a reddish-brown hue.

The hydrates are mostly compounds of metallic oxides with water; they are sometimes termed hydroxides, or hydrated oxides. (The word "hydroxide" is open to the objection that it infringes on the restriction of *ide* to the names of binary compounds.) Their formation is represented by the following equations :—

$$Na_2O \quad + \quad H_2O \quad = \quad 2NaHO.$$
Sodium oxide.   Sodium hydrate.

$$CaO \quad + \quad H_2O \quad = \quad CaH_2O_2.$$
Calcium oxide.   Calcium hydrate.
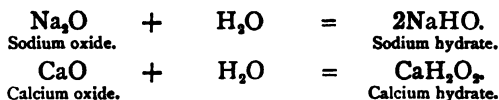
90. Salts.—When an acid and base react on each other, the body produced by the replacement of the hydrogen of the acid by the metal of the base is termed a salt. Water is also formed during the reaction. The action of the stronger acids and bases on each other is very violent; the resultant salts are usually without action on litmus. This is, however, not always the case; for when a strong acid combines with a weak base, the salt is acid to litmus : nitrate of mercury is an example. When the base is a strong one and the acid weak, as in sodium carbonate, the salt has an alkaline reaction. Litmus is itself a salt of a vegetable acid and base possessing a blue colour. An acid, when added, displaces the weak vegetable one, and forms a salt with the base; the litmus acid, being red, gives the solution a red tint. On adding a base it combines with the acid; the litmus acid and base being liberated again unite with the restoration of the blue colour. The following are instances of the formation of salts by the union of acids and bases :—

$$HCl \quad + \quad NaHO \quad = \quad NaCl \quad + \quad H_2O.$$
Hydrochloric acid.   Sodium hydrate.   Sodium chloride.   Water.

$$H_2SO_4 \quad + \quad CaO \quad = \quad CaSO_4 \quad + \quad H_2O.$$
Sulphuric acid.   Calcium oxide   Calcium sulphate.   Water.
(quicklime).

$$HCl \quad + \quad NH_4HO \quad = \quad NH_4Cl \quad + \quad H_2O.$$
Hydrochloric acid.   Ammonium hydrate.   Ammonium chloride.   Water.
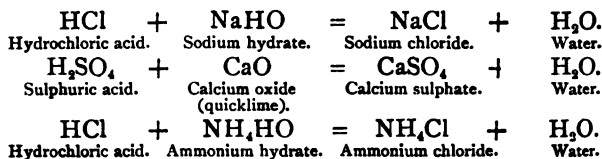
The acids are sometimes termed salts of hydrogen ; thus sulphuric acid would be called hydrogen sulphate.

Experiment 92.—Take a dilute solution of hydrochloric acid ; dip into it some paper coloured blue with litmus ; notice that the colour immediately changes to red. Dip this reddened paper in a solution of soda ; the blue colour is restored. Next add a few drops of litmus solution to the caustic soda in a large test-tube ; add the acid very carefully until the blue colour changes to a port-wine tint ; should this be overshot, the mixture becomes red ; a very small quantity of soda must then be added ; this will bring the colour back to the intermediate tint. It may be that a single drop of either reagent changes the colour from full blue to red, or *vice versâ;* if so, dilute down some acid with four or five volumes of water, and add this drop by drop ; with care the port-wine tint may be thus hit. Now dip in some red and blue litmus paper : the colour of neither is changed ; neither free acid nor alkali is present ; the whole of each has united to form the salt, sodium chloride. Evaporate to dryness : cubical crystals form.

Experiment 83, in which dry hydrochloric acid is passed over manganese dioxide, shows that water is formed as a secondary product by the mutual action of an acid and base. An interesting modification of the experiment may be tried by substituting lead oxide or litharge (PbO) for the manganese dioxide. On applying heat to the bulb the yellow litharge changes to white lead chloride, and abundance of water condenses in the second bulb according to the equation—

$$\underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Lead oxide.}}{PbO} = \underset{\text{Lead chloride.}}{PbCl_2} + \underset{\text{Water.}}{H_2O.}$$
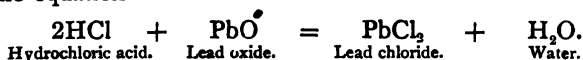
The oxides of zinc, copper, and in fact most other *metallic* oxides, interact in the same way as these with acids, forming their respective salts, with the separation of water in the free state.

91. Names of Acids and Salts.—The names of acids are derived from those of their principal constituents by changing them into adjectives ending in *ic ;* thus from

sulphur we have sulphuric acid, and from nitrogen, nitric acid. The hydracids are distinguished by the prefix *hydro*, as hydrochloric acid. The names of the corresponding salts are derived from the same root by adding *ate;* the salts of sulphuric and nitric acids are respectively sulphates and nitrates.

When an element forms two oxides, both of which unite with water to form acids, the acid containing the higher proportion of oxygen receives the name ending in *ic;* for the other the termination *ous* is substituted. There are, for instance, two oxides of sulphur, SO_2 and SO_3: these are termed—

$$SO_2, \text{ Sulphurous anhydride.}$$
$$SO_3, \text{ Sulphuric anhydride.}$$

Both combine with water, becoming—

SO_2	$+$	H_2O	$=$	H_2SO_3.
Sulphurous anhydride.		Water.		Sulphurous acid.
SO_3	$+$	H_2O	$=$	H_2SO_4.
Sulphuric anhydride.		Water.		Sulphuric acid.
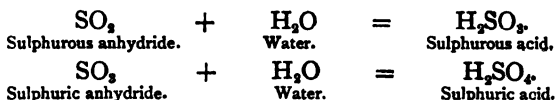
The salts of an acid whose name ends in *ous* have the termination *ite* :—

| H_2SO_3 | $+$ | $2NaHO$ | $=$ | Na_2SO_3 | $+$ | $2H_2O$. |
| Sulphurous acid. | | | | Sodium sulphite. | | |
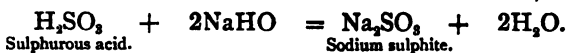
In describing the basic component of a salt, the simplest method is to mention the name as potassium sulphate. At times it is convenient to change this into the adjective form. When this is done, the same termination is used as is applied to the base itself; thus, salts formed by the action of mercuric oxide (HgO) on acids are called mercuric salts; those from mercurous oxide (Hg_2O), mercurous salts :—

HgO	$+$	$2HCl$	$=$	$HgCl_2$	$+$	H_2O.
Mercuric oxide.		Hydrochloric acid.		Mercuric chloride.		
Hg_2O	$+$	$2HCl$	$=$	Hg_2Cl_2	$+$	H_2O.
Mercurous oxide.		Hydrochloric acid.		Mercurous chloride.		
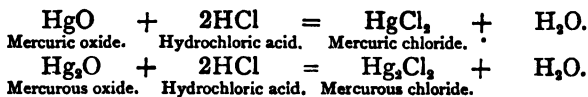
The salts of the hydracids, being binary compounds, have names ending in *ide.*

Summary.

Names of binary compounds end in *ide;* when the same elements form two, a separate name is given to each.

The most important compounds containing more than two elements are the acids ; the names of these are derived from the principal element.

92. Quantivalence.—The student already knows that the atom of chlorine combines with only one atom of hydrogen to form a molecule of hydrochloric acid; while one atom of oxygen combines with two of hydrogen to form a molecule of water. Remembering that the most trustworthy method of determining the molecular constitution of bodies is by an investigation of their densities, a study of the following table is exceedingly instructive :—

Column No. I. gives the name.

    ,,   II. The formula corresponding to the observed density.

    ,,   III. The molecular weight as deduced from the formula; that is, the sum of all the atomic weights.

    ,,   IV. The density as calculated from the molecular weight, being $\frac{1}{2}$ mol. wt.

    ,,   V. The density as determined experimentally.

An inspection of this table shows that first we have a group of molecules containing one atom only of each element, and representing therefore the simplest compounds possible. The elements, H, Cl, Br, and I are distinguished by this property of having their combining power in the gaseous molecule exhausted as soon as one of their atoms has combined with one atom of any other element. In the second class we have a series of elements, whose single

I. Name.				II. Formula.	III. Molecular weight.	IV. Calcd. density.	V. Observed density.
I.							
Hydrochloric acid	.	.	.	HCl	36·37	18·18	17·99
Hydrobromic acid	.	.	.	HBr	80·76	40·38	39·10
Hydriodic acid	.	.	.	HI	127·53	63·76	64·07
Iodine monochloride	.	.	ICl	161·9	80·95	—
Mercurous chloride	.	.	HgCl	235·2	117·6	120·49
II.							
Water	.	.	.	OH₂	OH$_2$	17·96	8·98	8·98
Sulphuretted hydrogen	.	.	SH₂	33·98	16·99	17·18
Cadmium bromide	.	.	CdBr₂	271·1	135·55	133·67
Mercuric chloride	.	.	HgCl₂	270·5	135·25	141·41
III.							
Boron chloride	.	.	.	BCl₃	117·0	58·5	58·00
Ammonia	.	.	.	NH₃	17·01	8·5	8·61
Phosphine	.	.	.	PH₃	33·96	16·98	17·03
Phosphorous chloride	.	.	PCl₃	137·07	68·53	70·42
Arsenious iodide	.	.	AsI₃	454·5	227·25	232·32
IV.							
Marsh gas	.	.	.	CH₄	15·97	7·98	8·03
Carbon tetrachloride	.	.	CCl₄	153·45	76·72	76·91
Stannic chloride	.	.	SnCl₄	258·9	129·45	132·95
V.							
Molybdenum chloride	.	.	MoCl₅	272·4	136·2	136·51
Tungsten pentachloride	.	.	WoCl₅	360·9	180·45	183·26
VI.							
Tungsten hexachloride	.	.	WoCl₆	396·2	198·1	190·47
I.							
Carbon monoxide	.	.	.	CO	27·93	13·96	13·96
Nitric oxide	.	.	.	NO	29·97	14·98	15·00
II.							
Nitrogen peroxide	.	.	.	NO₂	45·93	22·96	22·94
Nitrous oxide	.	.	.	ON₂	43·98	21·99	21·93
Sulphur dioxide	.	.	.	SO₂	63·90	31·95	32·46
Carbon dioxide	.	.	.	CO₂	43·89	21·94	22·07
Carbon disulphide	.	.	.	CS₂	75·93	37·96	38·09
III.							
Sulphur trioxide	.	.	.	SO₃	79·86	39·93	43·43
IV.							
Osmic anhydride	.	.	.	OsO₄	262·4	131·2	128·42

atoms combine with two atoms of members of the first group. In the third group we have elements combining with three such atoms, while in the fourth, fifth, and sixth, they combine respectively with four, five, and six first group atoms. The elements studied in the preceding table, at least, have different values of atom-combining power. **The measure of the number of atoms of other elements, with which one atom of each element can combine, is termed Quantivalence, or Atomicity.**

The quantivalence of each member of the first group is *one* in the particular compounds there given, and hence such elements are styled "monovalent or monads." The following nomenclature has been proposed to distinguish the various groups :—

Group I. Monovalent or Monads.
  „ II. Divalent   „ Dyads.
  „ III. Trivalent   „ Triads.
  „ IV. Tetravalent „ Tetrads.
  „   V. Pentavalent „ Pentads.
  „ VI. Hexavalent „ Hexads.

Examination of such a series of compounds as that we have been studying shows that a definite relation exists between the quantivalence of an element and its chemical equivalent and atomic weight. **The quantivalence of an atom represents the number of times the equivalent weight of the element is contained in its atomic weight.** Thus the atomic weight and equivalent of oxygen are respectively 15·96 and 7·98 ; and

$$\frac{15 \cdot 96}{7 \cdot 98} = 2,$$ which is the quantivalence of oxygen.

93. Graphic Notation.—The exact nature of the force by which the atoms of elements are bound together to form a compound is unknown to us ; but we see that we can attach a numerical value to such connecting or linking

power of each atom. Thus the atom of hydrogen has its combining capacity exhausted when it has united with one atom of another element : tungsten, on the other hand, does not suffer similar exhaustion until united directly with six atoms of some other element. This linking power is expressed graphically by attaching to the symbol of the element a number of lines each representing one link or unit of valency (atom-combining power). The following are examples of such graphic symbols :—

$$\text{H}— \qquad \text{Cl}— \qquad —\text{O}— \qquad \overset{\displaystyle |}{\underset{\displaystyle |}{—\text{B}—}}$$

Hydrogen.   Chlorine.   Oxygen.   Boron.

$$\overset{\displaystyle \backslash \; /}{\underset{\displaystyle / \; \backslash}{\text{C}}} \qquad \overset{\displaystyle \backslash \; /}{\underset{\displaystyle / \, | \, \backslash}{\text{P}}} \qquad \overset{\displaystyle \backslash \; /}{\underset{\displaystyle / \; \backslash}{—\text{Wo}—}}$$

Carbon.   Phosphorus.   Tungsten.
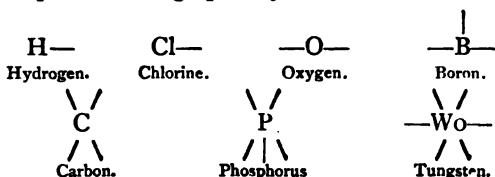
Adopting this system of notation it is an easy step forward to represent compounds by what are termed graphic formulæ, that is, formulæ in which the valency of each atom is shown by these graphic representations of lines, and the probable mode of linking in the various compounds by the disposition of these lines between the atoms. Thus we have the following examples of graphic formulæ :—

Hydrochloric acid,   H—Cl

Water,   H—O—H

Boron chloride,   Cl—B—Cl
$$\overset{\displaystyle |}{\text{Cl}}$$
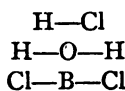
Carbon hydride (marsh gas), $\overset{\displaystyle \text{H} \quad \text{H}}{\overset{\displaystyle \backslash \; /}{\underset{\displaystyle / \; \backslash}{\underset{\displaystyle \text{H} \quad \text{H}}{\text{C}}}}}$

Molybdenum chloride, $\overset{\displaystyle \text{Cl} \quad \text{C}}{\overset{\displaystyle \backslash \; /}{\underset{\displaystyle / \; \backslash}{\underset{\displaystyle \text{Cl} \; | \; \text{Cl}}{\underset{\displaystyle \text{Cl}}{\text{Mo}}}}}}$

N

Tungsten hexachloride,

$$\begin{matrix} Cl & & Cl \\ & \diagdown & \diagup \\ Cl & \!\!-Wo-\!\! & Cl \\ & \diagup & \diagdown \\ Cl & & Cl \end{matrix}$$
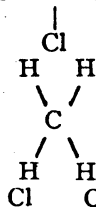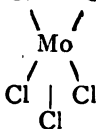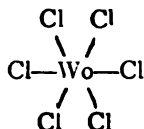
Graphic formulæ are explained at this stage because of the assistance they will render in the following paragraphs. One word of caution is perhaps necessary; the lines in graphic formulæ are only intended to indicate the number and disposition of the valencies of each atom. They must not be viewed as any representation of the actual position physically of the atoms in regard to each other. Thus tungsten chloride may be represented by either

$$\begin{matrix} Cl & & Cl \\ & \diagdown & \diagup \\ Cl & \!\!-Wo-\!\! & Cl \\ & \diagup & \diagdown \\ Cl & & Cl \end{matrix} \qquad \text{or} \qquad \begin{matrix} Cl \diagdown & & \diagup Cl \\ Cl \!\!-\!\! & Wo & \!\!-\!\! Cl \\ Cl \diagup & & \diagdown Cl \end{matrix}$$
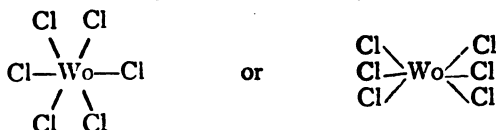
The position and length of the links is merely a matter of convenience at the time of writing the formula.

94. Variable Quantivalence.—Examination of the table in the last but one paragraph shows that different elements appear in more than one class; thus mercury forms two chlorides and bromides, being a monad in the one series and a dyad in the other. Tungsten also forms two distinct chlorides, in which it is pentavalent and hexavalent respectively. We therefore see that the number of atoms of other elements with which the atom of one element combines is not absolutely constant. The question arises whether in such different compounds the actual valency or quantivalence of the element has changed, or that the valency is in the one case unsatisfied. Thus, taking the two mercury chlorides must the graphic formulæ be written—

Hg—Cl and Cl—Hg—Cl
or
—Hg—Cl and Cl—Hg—Cl ?
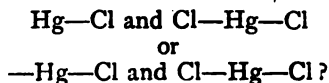
As a result of investigations of such series of compounds, abundant evidence has been accumulated which shows that in cases where an element has different valencies in different compounds, in the lower members of such series an unsatisfied valency exists. This is exhibited by the ease with which the compound assimilates additional atoms by which its normal or higher valency is fully engaged. It is perfectly competent for an element to form a compound in which a portion of its valency remains unsatisfied, but such compounds usually combine readily with additional atoms.

An inspection of our table, p. 175, shows that the valency of an element is usually the same by whichever of the monad elements it may be measured. For example, whether H, Cl, or Br be taken as the unit, we find that combination is with the same number of atoms of each; thus we have, BF_3 and BCl_3; PH_3 and PCl_3; CH_4 and CCl_4.

The next question is whether elements exhibit the same valency towards a dyad as a monad element; thus should the divalency of an oxygen atom be equally satisfied with the divalency of another dyad atom, as it is with the valencies of two monad atoms? In answer to this question, the student is referred to the second part of our table, in which such compounds, containing polyvalent atoms, as have had their molecular weight satisfactorily determined, are inserted.

Examining this table we find that carbon combines with two atoms of oxygen and of sulphur as against four of hydrogen or chlorine, a fact expressed in the following graphic formulæ :—

```
   H   H
    \ /
     C            O=C=O.
    / \
   H   H
```

```
Cl   Cl
 \  /
  C              S=C=S.
 /  \
Cl   Cl
```
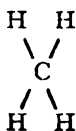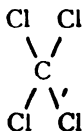
So far it would seem that the tetravalent atom of carbon has its valencies equally satisfied with either four atoms of a monad or two of a dyad; but there is not the same uniformity throughout, three gaseous compounds of nitrogen with oxygen are given, and in no case does the valency agree with that of nitrogen in its compound with hydrogen, NH_3 (ammonia). Indicating the valencies by graphic formulæ, we have—

```
H—N—H
    |
    H
—N=O      O—N=O      =N—O—N=
```
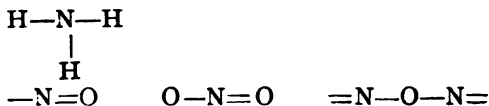
In each of the three cases, there are unsatisfied links, and in that of NO_2, in which nitrogen figures as a triad, there is one oxygen link unattached. According to its hydrogen valency, nitrogen should combine with oxygen in the proportion of one atom of nitrogen to one and a half of oxygen (in whole numbers, 2 to 3), whereas in this particular compound the proportion is one to two.

Apart from irregularities of the kind just described, examination shows that a number of elements have greater relative combining powers with oxygen than with hydrogen or the monads. Thus nitrogen combines with three atoms of hydrogen, and with two atoms of oxygen. Sulphur combines with two atoms of hydrogen, forming respectively SH_2; but with oxygen it produces the following compounds, in which sulphur must be represented as possessing a much higher valency—sulphur dioxide, SO_2, and sulphur trioxide, SO_3. Further investigation would show that several other elements have a higher relative combining power with oxygen than with the monad hydrogen.

The valency of the atoms in solid molecules is not capable of determination with the same accuracy as can be done with those which can be examined in the gaseous state. In the Table of Elements inserted in Chapter III. the probable maximum valencies are given.

95. Odd and Even Valencies.—Examination of a number of series of compounds shows that in many instances the active valency of an element increases or diminishes by two. Thus we have carbon monoxide, CO, and carbon dioxide, CO_2; phosphorus chloride, PCl_3, and phosphorus fluoride, PF_5. Making use of graphic formulæ, the free or unsaturated valencies of the lower compounds of these two pairs are represented by—

$$=C=O \quad \text{and} \quad =P\underset{\diagdown Cl}{\overset{\diagup Cl}{\leftarrow Cl}}$$
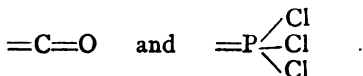
It has been assumed that in such cases the units of valency combine with each other in pairs, and so become latent. Under this hypothesis the active valency of an element must be represented by either an even or an odd number, and accordingly the elements have been divided into *perissads* whose valency is odd, and those having even valencies, which are termed *artiads*. The classification has, however, dropped into disuse, because in the first place the number of free valencies in unsaturated compounds is not always represented by an even number (tungsten, for instance, is both perissad and artiad in its chlorides); secondly, there is not sufficient proof that such union between the valency links does take place. The frequency with which active valency increases or diminishes by two may be partly accounted for by the fact that oxygen and some other of the most commonly occurring elements are dyads. Whenever a single atom of an element forms two or more oxides the valency must increase or diminish by two; thus we have barium oxide and peroxide, lead oxide and peroxide,

and sulphur dioxide and trioxide, all of which are examples of the case in point.

$$Ba{=}O \quad \text{and} \quad O{=}Ba{=}O$$
$$Pb{=}O \quad \text{,,} \quad O{=}Pb{=}O$$
$$O{=}S{=}O \quad \text{,,} \quad O{=}S{=}O$$
$$\overset{\|}{O}$$
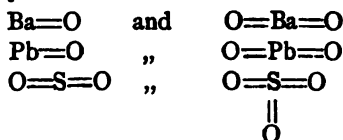
The above graphic formulæ show the increase in valency in each of the pairs of compounds.

96. Basicity of Acids.—In the formation of salts, the hydrogen of an acid is replaced by a metal. Hydrogen, being monovalent, is replaced by different metals in proportions varying according to their valency. The valency of the displacing metals must be equal to that of the total number of atoms of hydrogen displaced. Thus a monad metal will replace one atom of hydrogen; a dyad, two atoms, and so on. **The quantity of a base required to form a salt with an acid depends on the number of atoms of hydrogen present capable of replacement by the base; the measure of this quantity is termed the "basicity" of the acid.** Those acids containing but one atom of replaceable hydrogen are termed monobasic, those with two and three such atoms are known respectively as dibasic and tribasic acids.

A monobasic acid requires one atom of a monad metal to form a salt, while with a dyad metal, two molecules of the acid are necessary. In every case such number of molecules of acid and atoms of metal must be taken as will give the same total valency of replaced hydrogen atoms as that of the replacing metal. In the following table typical examples are given of the formation of salts:—

<div align="center">MONOBASIC ACID.</div>

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Sodium hydrate.}}{NaHO} = \underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{}{2HNO_3} + \underset{\text{Calcium hydrate.}}{CaH_2O_2} = \underset{\text{Calcium nitrate.}}{Ca(NO_3)_2} + 2H_2O.$$

$$3HNO_3 \quad + \quad \underset{\text{Bismuth hydrate.}}{BiH_3O_3} \quad = \quad \underset{\text{Bismuth nitrate.}}{Bi(NO_3)_3} \quad + \quad 3H_2O.$$

DIBASIC ACID.

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} \quad + \quad 2NaHO \quad = \quad \underset{\text{Sodium sulphate.}}{Na_2SO_4} \quad + \quad 2H_2O.$$

$$H_2SO_4 \quad + \quad CaH_2O_2 \quad = \quad \underset{\text{Calcium sulphate.}}{CaSO_4} \quad + \quad 2H_2O.$$

$$3H_2SO_4 \quad + \quad 2BiH_3O_3 \quad = \quad \underset{\text{Bismuth sulphate.}}{Bi_2(SO_4)_3} \quad + \quad 6H_2O.$$

TRIBASIC ACID.

$$\underset{\text{Phosphoric acid.}}{H_3PO_4} \quad + \quad 3NaHO \quad = \quad \underset{\text{Sodium phosphate.}}{Na_3PO_4} \quad + \quad 3H_2O.$$

$$2H_3PO_4 \quad + \quad 3CaH_2O_2 \quad = \quad \underset{\text{Calcium phosphate.}}{Ca_3(PO_4)_2} \quad + \quad 6H_2O.$$

$$H_3PO_4 \quad + \quad BiH_3O_3 \quad = \quad \underset{\text{Bismuth phosphate.}}{BiPO_4} \quad + \quad 3H_2O.$$

97. Acid, Normal, and Basic Salts.—Salts such as those whose formulæ are given in the preceding table are termed normal salts. **A normal salt may be defined as that produced by the replacement of the hydrogen of the acid by its valency equivalent of a metal**, or group of elements functioning as a metal, in a base.

In the case of those acids which contain more tnan one atom of replaceable hydrogen, a portion only of such hydrogen is sometimes replaced; the result is a salt still possessing an acid character. **An "acid" or "hydric" salt is defined as that produced by the replacement of a portion only of the hydrogen of a polybasic acid by the metal of a base.** Acid sodium sulphate, $NaHSO_4$, is an example of a hydric or acid salt.

There are certain oxy-acids which possess the power of combining with more of the base than is necessary to produce a normal salt, thereby forming what are known as basic salts. **A "basic" salt is defined as that produced by the combination of an acid with a higher proportion of a base than is necessary for the formation of a normal salt.** The following is an example of a basic salt; the

additional quantity of base being distinguished by being placed outside a comma in the formula :—

Basic mercury sulphate (turpeth mineral), $HgSO_4,(HgO)_2$.

98. Acidimetry and Alkalimetry. — Among the various operations of analysis one most important series is that dealing with the estimation of the quantities of acid or alkali in various substances. The general principle adopted is that of adding, to a measured quantity of the substance, acid or alkali solution of known strength until the point of neutrality is reached. The test solutions are added from graduated measuring vessels termed burettes, and the neutral point is determined by the use of some indicator, the best known being litmus, methyl-orange, and phenol-phthalein.

Litmus solution is turned red by acids, and has its blue colour restored by alkalies.

Methyl-orange is employed in solution in alcohol, and in alkaline solutions has a yellow tint, which changes to pink or red with the slightest excess of acid. Methyl-orange is absolutely unaffected by carbonic acid, and for that reason is of considerable value in certain estimations.

Phenol-phthalein is more sensitive than litmus, and in an acid solution produces no colour, but with the slightest excess of alkali an intense magenta-red is produced.

For acidimetry and alkalimetry a series of standard solutions is prepared. These are commonly of the strength known by analysts as *normal* solutions. The normal acid solutions are prepared so that at 16° C. one litre shall contain 1 gram of the replaceable hydrogen of the acid. Consequently normal sulphuric acid solution must contain—
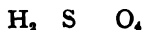
H_2 S O_4
$(2 + 32 + 64 = 98) \div 2 = 49$ grams per litre $= 0.049$
       gram per c.c.

Similarly normal hydrochloric acid must contain—

H   Cl

$1 + 35.37 = 36.37$ grams per litre $= 0.036$ gram per c.c.

The normal alkali solutions must contain per litre the chemical equivalent, weighed in grams of the hydrogen-replacing metal or group of elements. Thus normal sodium hydrate solution must contain—

Na   H   O.

$23 + 1 + 16 = 40$ grams per litre $= 0.040$ gram per c.c.

(Sodium and hydrogen are equivalent to each other, atom for atom.)

Normal barium hydrate (BaH_2O_2) solution must contain

Ba H_2 O_2
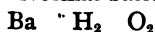
$(137 + 2 + 32 = 171) \div 2 = 85.5$ grams per litre $= 0.085$ gram per c.c.

(The chemical equivalent of barium is half its atomic weight.)

Equal quantities of any normal acid and alkali solution exactly neutralize each other; and the quantity of any solution of a single acid or alkali which is neutralized by 1 c.c. of a normal solution contains 0·001 gram of the hydrogen equivalent of its active constituent. The analyst makes use of a table giving the weights of actual substance in each case, corresponding to the hydrogen equivalent.

Experiment 93.—Procure some standard normal solutions of sulphuric acid and sodium hydrate respectively. (These may be prepared in the laboratory according to the directions given in works on analysis, or may be purchased from dealers in chemicals.) There will also be required a double burette-stand and two burettes, each of 50 c.c. capacity. A burette consists of a glass tube open at the top and drawn to a small end at the bottom ; over this is drawn a piece of indiarubber tube with a small glass dropping tube at the bottom. A spring clip permits the bottom of the burette to be opened or closed. The

instrument is graduated throughout most of its length, having the zero at the top and the scale of figures descending.   The lower end of such a burette is shown in Fig. 41.   Carefully clean the

two burettes, and allow them to drain.   Rinse the one with a few drops of normal acid solution, place it in the burette-stand, and then fill it to above the zero mark at the top.   Rinse and subsequently fill the other in the same manner with normal soda (sodium hydrate) solution.   Press the buttons of the spring clip in each case until the liquid runs down to the zero mark. Next pour about 50 c.c. of distilled water in a clean porcelain basin about 4 inches diameter, and run into it from the burette 10 c.c. of normal acid solution.   Add two or three drops of phenol-phthalein solution ; there is no colour produced.   Read off the height of the soda solution in the burette (zero to start with), and make a note. Then, without consulting the graduations, run in soda until one drop imparts a red colour to the solution.   Read off the height of the soda in the burette ; there ought to be exactly 10 c.c. run in to neutralize the acid.

FIG. 41.—Burette with spring clip.

In the next place, ask some one else to run the acid into the beaker, without yourself knowing the quantity.   Test with soda solution as before, reading off the height in the burette before commencing to add the solution, and again as soon as the red colour is produced.   Try whether the quantity thus found agrees with that which had been added.

Make a similar determination of alkali by working on an unknown quantity and adding acid till the colour of the phenolphthalein disappears.

Next determine the percentage of sulphuric acid in a dilute solution of unknown strength.   Take a small beaker, wipe it carefully dry, and weigh on the delicate balance.   Pour into it about 10 c.c. of the dilute acid, and again weigh carefully.   Add

some distilled water and two or three drops of phenol-phthalein, and then "titrate" with normal soda. Calculate the percentage of acid present. The verb "titrate" means to measure by means of solutions of known strength, such as are here being employed.

In the next place, determine the percentage of sodium hydrate in a similar manner in a dilute solution of unknown strength, titrating with normal sulphuric acid.

Next determine the percentage of sodium carbonate in a sample of common washing soda. Weigh off exactly about 2 grams of the soda, and dissolve in about 50 c.c. of distilled water in a small beaker; add two or three drops of methylorange, and titrate with normal acid until the yellow tint changes to red. With each addition of acid there is an effervescence of carbon dioxide gas, but this does not interfere with the estimation. Calculate what percentage of pure anhydrous sodium carbonate, Na_2CO_3, and of the crystallized carbonate, Na_2CO_3, $10H_2O$, is present.

The calculations are best made clear by means of examples. The following are results obtained in the author's laboratory :—

DETERMINATION OF SULPHURIC ACID.

Weight of beaker and acid . . .	39·43 grams.
Weight of dry beaker	27·76 ,,
Weight of acid taken . . .	11·69 ,,
Final reading of burette . . .	23·6 c.c.
First reading of burette	9·2 ,,
Soda solution taken for neutralization	14·4 ,,

Normal soda and acid are equivalent to each other, and therefore 11·69 grams of the acid solution to be tested contains sulphuric acid equal to the quantity in 14·4 c.c. of standard acid; that is—

$$14·4 \times 0·049 = 0·7056 \text{ gram.}$$

Then—

As $11 \cdot 69 : 100 :: 0 \cdot 7056 : 6 \cdot 04$ = per centage of sulphuric acid in the solution.

DETERMINATION OF SODIUM CARBONATE.

Weight of washing soda taken   .   .   . $2 \cdot 13$ grams.

Final reading of burette   .   .   .   . $37 \cdot 3$ c.c.
First reading of burette   .   .   .   . $24 \cdot 2$,,
     Acid taken for neutralization   .   . $13 \cdot 1$,,

It is first necessary to decide what quantity of sodium carbonate is equivalent to the normal solution of sulphuric acid. The following are the formulæ and molecular weights of the anhydrous and crystallized carbonates respectively:—

$$\begin{array}{ccc} Na_2 & C & O_3 \\ 46 + 12 & + & 48 = 106. \end{array}$$
$$\underbrace{Na_2CO_3}_{106} \quad \begin{array}{cc} 10 & H_2O \\ + (10 \times 18 =) \ 180 = 286. \end{array}$$
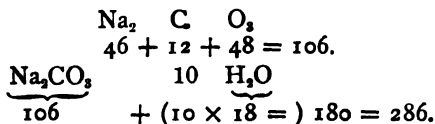
As the molecule contains twice the sodium equivalent, it is evident that half these quantities, namely, 53 grams per litre for the anhydrous and 143 for the crystallized carbonates, are the strengths for normal solutions equivalent to those of other acids and alkalies. From this it follows that the values per c.c. are respectively $0 \cdot 053$ and $0 \cdot 143$ grams. The acid taken for neutralization is therefore equivalent to—

$13 \cdot 1 \times 0 \cdot 053 = 0 \cdot 694$ grams of Na_2CO_3.
$13 \cdot 1 \times 0 \cdot 143 = 1 \cdot 873$,, $Na_2CO_3, 10H_2O$.

From these the percentages are readily calculated—

As $2 \cdot 13 : 100 :: 0 \cdot 694 : 32 \cdot 58$ per cent. of Na_2CO_3 in sample.
As $2 \cdot 13 : 100 :: 1 \cdot 873 : 87 \cdot 93$,,   of $Na_2CO_3, 10H_2O$ in sample.

Then $100 - 87\cdot93 = 12\cdot07$ per cent. of water or other impurities present.

(NOTE.—This sample had been purposely adulterated by the addition of common salt.)

Summary.

The atoms of different elements have a varying combining power; the measure of such is termed "quantivalence." Graphic notation is employed to show symbolically the valency of atoms in formulæ. The quantivalence of the atoms of certain elements varies, both in regard to different other elements, and in many cases also in regard to one and the same other element. Classification into odd and even valencies is comparatively devoid of significance. The basicity of acids is a measure of the replaceable hydrogen contained by the acid. Salts are classified into acid, normal, and basic salts. Acids and alkalies are estimated in analysis by means of alkaline and acid solutions of fixed strength; the operation of so measuring is termed "acidimetry," or "alkalimetry," as the case may be.

LABORATORY DIRECTIONS.

Methyl-orange is a yellowish-brown powder, and is prepared for use by dissolving one part in thirty parts of strong alcohol (methylated spirits). Phenol-phthalein is also a brownish powder, and is prepared for use in a similar manner.

In most laboratories, normal sulphuric acid and sodium hydrate solutions obtain a place among the reagents. Directions are given in works on analysis for their preparation, but, failing these, they may be obtained from dealers in chemicals. Burettes should be carefully washed after each time of being used. In reading the height of the acid or alkali in the burette, it will be observed that the liquid has a curved surface. This curve is known as a meniscus, and in reading, the position of the bottom of the meniscus is taken. In reading, have the eye as nearly as possible on the same level as the meniscus, and place the burette facing a window.

CHAPTER XII.

CARBON.

Symbol, C. Atomic weight, 11·97. Specific gravity, as diamond, 3·3 to 3·5.

The specific gravity of solids and liquids is referred to that of water, which is taken as unity.

99. Occurrence.—Two well-marked crystalline modifications of carbon occur naturally in the free state, being known respectively as diamond and graphite. In addition to these, carbon is an essential constituent of all compounds of organic origin, from which bodies it may be obtained in the amorphous condition; such carbon is termed charcoal or coke, according to the source from which derived. Limestone, chalk, and other natural carbonates also contain carbon in enormous quantities.

100. Preparation.—By heating wood, coal, or bones in a closed vessel, carbon in an impure state may be obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other body.

Experiment 94.—Fit up the apparatus shown in Fig. 14 with a combustion tube; place in it some chips of dry wood; fix the tube in the retort stand with the mouth slightly lower than the other end, so that any liquid which distils may not run back on the hot glass. Place a bottle for the collection of the gas, and apply heat to the wood: some water and a tarry liquid

condense in the cooler part of the tube ; an inflammable gas passes over into the jar. When the action ceases, a black mass remains of approximately the same shape as the original wood, and still retaining the grain and marks of the woody structure : this body is charcoal.

This process of heating a body and causing its decomposition into gaseous and liquid products in part, which are collected, is termed " destructive distillation."

Charcoal is manufactured sometimes in this way, in large iron retorts, but more frequently by building a mass of wood faggots, covering them with peat, and making an opening at the top and bottom. The pile is then fired, a portion only of the wood is allowed to burn, and its heat converts the remainder into charcoal.

Coal is subjected to destructive distillation on the large scale for the manufacture of coal-gas; the carbon which remains in the retort is known as "coke." It is denser and harder than wood charcoal.

Bones, on being similarly treated, yield "animal charcoal." This, when finely ground, is called "ivory black."

A purer form of charcoal is obtained by burning turpentine, resin, or other substances rich in carbon. With a limited supply of air the hydrogen burns, and the carbon, being liberated, is deposited as soot in chambers arranged for its collection. In this way lampblack is made. It, however, still contains hydrogen, which is driven off by heating the lampblack intensely in a current of chlorine. Hydrochloric acid is formed, and carbon remains. The carbon obtained by the whole of these methods is amorphous ; graphite and diamond are both crystalline. Graphite occasionally crystallizes out in small hexagonal plates from the solution of carbon in fused cast iron. Chemists have long sought to obtain crystals of diamond by artificial means, but hitherto without success.

101. Properties.—The three forms in which carbon

occurs differ remarkably in appearance and physical properties.

102. Diamond.—The diamond is usually found in rounded pebbles, but sometimes occurs in well-developed crystals of octahedral form, or shapes closely allied to it. Fig. 42 is an illustration of an octahedron. The lozenge-shaped outline of this figure, when viewed in certain directions,. is familiar to all under the name of "diamond-shaped." The diamond is the hardest substance known, scratching or cutting all other bodies. Small crystals set in a proper holder are used by glaziers for cutting glass. When pure the diamond is perfectly transparent and colourless; it takes a very high polish. Its index of refraction is high (that is, a ray of light which enters it obliquely is bent very considerably). Owing to this fact much of the light undergoes total reflection, and this is one cause of its great brilliancy when cut and used as a gem. The diamond neither conducts electricity nor heat. It may be made red hot without change; but in the intense heat of the voltaic arc it swells up, becomes opaque, and is changed into a black coke-like mass, and acquires the power of conducting heat and electricity.

FIG. 42.—Model of Octahedron.

103. Graphite.—Graphite differs from the diamond in almost every characteristic. It occurs in compact masses, which appear to be more or less crystalline. The more perfect crystals occur as hexagonal plates. This crystalline shape is totally distinct from that of the diamond. Graphite has a metallic lustre, and is of a leaden-grey colour; it has consequently also received the names plumbago and black lead. It is very soft, and marks paper. The finer qualities are employed in the manufacture of black-lead pencils; it has a peculiar greasy feel, and is sometimes employed for

lessening the friction between two rubbing surfaces. After the metals, graphite is one of the best conductors of heat and electricity.

104. Amorphous Carbon.—Amorphous carbon or charcoal possesses a remarkable property of absorbing gases and condensing them within its pores. Freshly burnt charcoal is in this way capable of absorbing about ninety volumes of ammonia. This property is demonstrated by experiment in the chapter on that gas. Owing to this peculiar property charcoal is a valuable antiseptic: it absorbs various putrefactive gases, and thus brings them into contact with oxygen, also condensed within it. Oxidation proceeds, and these gases, which are mostly composed of hydrogen and carbon, are changed into harmless and odourless compounds, viz. water and carbon dioxide.

Charcoal also retains the colouring matter of liquids passed through it. Raw sugar is decolorized by being mixed in solution with animal charcoal and then filtered; the filtrate is found to be colourless.

Experiment 95.—Take some syrup of the brownest and coarsest sugar obtainable , shake up in a test-tube with coarsely powdered animal charcoal ; allow the charcoal to subside and then filter off; the sugar solution will be much lighter in colour. The colour of the original solution may, if necessary, be heightened by the addition of a little burnt sugar.

In the form of lampblack, charcoal is used as the basis of printers' ink and other black pigments.

Another most important use of charcoal is in the manufacture of gunpowder.

105. Common Chemical Properties.—It is commonly stated that all forms of carbon are incapable of liquefaction or volatilization at the most intense heats at our command; but Despretz found that the heat produced by the passage of an intense electric current between carbon

o

points enclosed within an exhausted receiver, volatilized a portion of the carbon as a black cloud, which deposited itself in a crystalline form on the glass walls of the vessel. All varieties of carbon are combustible ; and the same weight of diamond, graphite, and charcoal yields the same amount of carbon dioxide when burned, thus establishing their chemical identity :—

$$C \quad + \quad O_2 \quad = \quad CO_2.$$

Carbon (diamond, graphite, or charcoal).   Oxygen.   Carbon dioxide.

The diamond may be burned by placing it on a connecting strip of platinum foil, between two copper wires passing through the stopper of a gas-jar filled with oxygen. The passage of a voltaic current raises the platinum to a white heat ; the diamond burns away, leaving only a minute trace of ash.

Graphite in the massive form may be burned more easily.

Experiment 96.—Fill a jar with oxygen ; place some powdered graphite in a clean deflagrating spoon ; ignite to a bright red heat over the foot blowpipe, and quickly plunge into the gas. Notice a brightening of the glow on entering the oxygen. When the action is over, take out the spoon, add lime-water and shake up ; the lime-water becomes milky.

Charcoal burns in oxygen with readiness.

Experiment 97.—Place a piece of charcoal in the deflagrating spoon, kindle it, and introduce into a jar of oxygen ; it burns brightly. Test the gas with lime-water and note milkiness.

Lime-water is prepared by adding a small piece of lime to water, and shaking up in a stoppered bottle. When the excess of lime has settled to the bottom, the clear solution is poured off, and is ready for use.

Lime and carbon dioxide combine readily and produce an insoluble substance, carbonate of lime ; hence the

milkiness. After a time this falls to the bottom as a white precipitate.

$$CaH_2O_2 \ + \ CO_2 \ = \ CaCO_3 \ + \ H_2O.$$

Calcium hydrate   Carbon dioxide.   Calcium carbonate   Water,
(lime-water),   carbonate of lime).
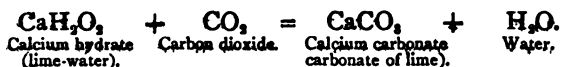
From this property lime-water is a most useful test for the presence of carbon dioxide. If the carbon dioxide is in considerable excess, the precipitate will re-dissolve.

Bodies containing carbon also yield carbon dioxide when burned.

Experiment 98.—Light a taper and place it in a jar of air ; when the light is extinguished, test with lime-water for carbon dioxide. Pour a few drops of methylated spirits in a deflagrating spoon ; light and place in a jar of air ; again test for carbon dioxide. Similarly pour a few drops of petroleum into the deflagrating spoon and heat until the liquid takes fire ; introduce into a jar of air, and test with lime-water.

Burn a small jet of coal gas in a jar of air, using the same apparatus as was employed for the burning of hydrogen in chlorine ; as soon as the light goes out, remove the gas jet and test with lime-water.

In each case carbon dioxide is found to be present. Water is also formed as a product of combustion of these bodies, all of which are compounds containing carbon and hydrogen. The formation of water is demonstrated by the quantity deposited when a cold body is placed above a gas flame. This may be observed whenever a flask of water is heated over a Bunsen. Water would also be deposited on the outside of a flask held over the chimney of a petroleum lamp. The carbon compounds with hydrogen are so universally used as heat-producers that no fuel could be taken which did not give these reactions.

Further than this, animal heat is also a result of the slow combustion of compounds of carbon. That articles of food contain carbon may be easily demonstrated.

Experiment 99.—Take small portions of bread, sugar, and

meat ; dry them and heat to redness in test-tubes of combustion tubing ; a mass of more or less pure carbon remains.

Finely powder each of these bodies in the dry state, and mix each with powdered copper oxide. Heat each mixture to redness in a combustion test-tube, fitted with cork and tube leading into lime-water. A milkiness is produced in each case, showing that their oxidation had produced carbon dioxide.

The carbon of food is assimilated by the stomach, and helps to build up the body. During the act of breathing, air is drawn into the lungs, and by certain indirect processes oxidizes certain constituents of the body, which are obtained from food. Water and carbon dioxide are thus produced, and are exhaled continually from the lungs.

Experiment 100.—Breathe against any cold surface, as the outside of a bottle of water ; it is covered with a film of dew. Breathe though a glass tube into some lime-water in a beaker ; it rapidly becomes milky.

Carbon dioxide is always present in the atmosphere as a result of these changes. Its presence may be detected by means of lime-water.

Experiment 101.—Partly fill an evaporating basin with lime-water, and let it remain exposed to the air for a few minutes ; a thin film of carbonate of lime will have formed on the surface.

That air contains far more carbon dioxide when exhaled from the lungs than when inspired may be proved by the following experiment :—

Experiment 102.—Fit up two wash-bottles such as are shown in No. 3, Fig. 18. By means of indiarubber tubing connect one end of a **T** or three-way tube with the long tube of one of the wash-bottles, and the second end of the **T** tube with the short tube of the other wash-bottle. About a quarter fill each wash-bottle with lime-water and insert the corks. Place the third limb of the **T** tube in the mouth and breathe ; as each breath is drawn in, air enters through the short-limbed wash-bottle, bub-bling through the lime-water. At each exhalation air passes out

through the other bottle. ·The air is thus passed through lime-water before and after being breathed. The lime-water in the first bottle is only rendered very slightly turbid ; that in the second rapidly becomes milky.

The functions of atmospheric carbon dioxide are treated more fully in Chapter XV.

. **106. Reducing Power of Carbon.**—Although carbon does not take fire at anything like so low a temperature as phosphorus and many other substances, it is yet a most powerful reducing agent. Its vigour as such increases with the temperature. At a bright red heat it decomposes phosphorus compounds, ·with the liberation of free phosphorus. Carbon also reduces, at a high temperature, the compounds of sodium and potassium, and thus enables those elements to be obtained in the metallic state. In the procuring of most metals from their ores, carbon not only acts as a fuel, producing the requisite amount of heat, but also serves as a reducing agent, combining with the oxygen or other element with which the metal is united in the ore.

Summary.

Carbon occurs in three forms : the diamond, graphite, and amorphous carbon as charcoal. The two first are native ; the third is obtained from certain organic bodies by heating them in closed vessels. The diamond is extremely hard ; graphite is soft and metallic-looking. Charcoal is used as a deodorizing and decolorizing agent. The whole three forms are combustible, producing carbon dioxide. This gas is detected by its turning lime-water milky. All bodies containing carbon produce carbon dioxide when burned ; carbon dioxide is also formed by animals breathing ; it is always present in air. Carbon is a most useful reducing agent.

OBJECT DEMONSTRATION.

Note the appearance and physical characters of specimens of diamond, graphite, coke, charcoal from various sources, and "gas carbon ; " also chalk, limestone, marble, and crystalline

Iceland spar as examples of natural carbonates. Examine a set glazier's diamond; also, if procurable, specimens of boring diamond (boart), particularly if set in a boring tube.

Study the shape and geometric characters of models of the octahedron and hexagonal prism.

LABORATORY DIRECTIONS.

After Exp. 94, clean the leading tube at once by passing water through it ; the tarry liquid is more difficultly removed after standing. Do not use any indiarubber tubing, but let the leading tube be entirely of glass.

In burning coal gas in a jar of air the jet must be removed as soon as the light goes out, because, if allowed to remain, the coal gas would displace the remaining air and carbon dioxide.

CHAPTER XIII.

Two oxides of carbon are known—

Carbon monoxide or carbonic oxide, CO.

Carbon dioxide or carbonic anhydride, CO_2.

The latter of these, being the most important, should be first studied.

Carbon Dioxide.—Formula, CO_2. Molecular weight, 43·89. Density, 21·94. Specific gravity, 1·527.

Graphic formula, $O{=}C{=}O$.

107. Occurrence.—The presence of carbon dioxide in the atmosphere is mentioned in the previous chapter; it also exists in vast quantities in combination with lime, in limestone, chalk, marble, etc.

108. Preparation.—By the action of heat, limestone may be decomposed into lime and carbon dioxide, according to the following equation :—

$$CaCO_3 \quad = \quad CaO \quad + \quad CO_2.$$
Limestone (calcium carbonate).   Lime (calcium oxide).   Carbon dioxide.
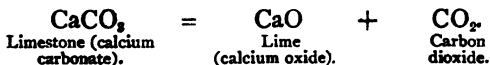
Enormous quantities of limestone are "burned" in properly constructed furnaces called kilns, for the purpose of obtaining quicklime, that substance being used in making mortar. The student may separate the two on the small scale in the following manner :—

Experiment 103.—In a test-tube of hard glass tubing place

a little powdered marble or chalk ; close the mouth of the tube loosely with the thumb, and heat strongly for about a minute over the foot blowpipe. Keep the tube closed, and pour into another test-tube some lime-water ; the gas being heavier than air, pour it from the combustion-tube into that containing the lime-water ; shake up : the lime-water becomes milky.

If the application of heat be continued, the whole of the carbon dioxide may be driven off; but in the time mentioned a part only will probably be evolved.

A much readier method of separating the carbon dioxide from the base is by the addition of an acid, as hydrochloric. The following change ensues :—

$$CaCO_3 \;+\; 2HCl \;=\; CaCl_2 \;+\; H_2O \;+\; CO_2.$$

<div align="center">

Calcium   Hydrochloric   Calcium   Water.   Carbon
carbonate.   acid.   chloride.   dioxide.

</div>

Experiment 104.—Add a drop of hydrochloric acid to lime-water which has been rendered milky by carbon dioxide ; it immediately becomes clear. Add some hydrochloric acid to some fragments of marble in a test-tube ; brisk effervescence occurs. When over, pour the gas, and the gas only, into a second tube containing lime-water ; this, on shaking, becomes milky.

Experiment 105.—Prepare four jars of the gas in the following manner. Place some fragments of marble or limestone in the flask arranged as for the preparation of hydrogen ; add a little water, and then some hydrochloric acid ; collect over water in the pneumatic trough.

109. Properties.—Carbon dioxide is a colourless gas. It has a faint, sweetish, acid taste and smell, which are best described as being those of a bottle of soda-water when opened (so-called soda-water is a solution of carbon dioxide in water under pressure).

At a pressure of 38·5 atmospheres this gas condenses to a liquid at 0° C. : it may also be liquefied at ordinary pressures by a temperature of −78° C. Liquid carbon dioxide is colourless and transparent ; on being allowed to emerge in a stream from the vessel containing it, a part volatilizes,

and, in so doing, deprives the remainder of the heat necessary to maintain it in the liquid state; it therefore freezes. Solid carbon dioxide obtained in this manner is a white, snow-like mass, which evaporates comparatively slowly.

At 15° C. the gas is soluble in about its own volume of water, whatever the pressure; but as an increase of pressure increases the density of the gas, the *weight* absorbed is in direct proportion to the pressure to which the gas is subjected. Soda-water, lemonade, and other aërated beverages, are prepared by dissolving carbon dioxide in water, under the pressure of a force-pump. From the solubility of the gas in water, directions are frequently given for its collection by displacement, but the gas is obtained so readily in large quantity that for most purposes it may as well be collected over water.

The weight of carbon dioxide permits many striking experiments to be performed with it.

Experiment 106.—Fill by downward displacement a bowl or some other vessel about 8 inches diameter, and the same depth, with the gas. Make a soap solution, and blow some bubbles; detach them from the pipe used over the vessel of gas; they will descend and float on the surface of the carbon dioxide.

This gas is generated in brewing. The vats remain full for some time after the liquor has been drawn off; and many deaths have occurred through men incautiously descending in them. The same danger exists from accumulations of the gas in mines. A lighted taper is instantly extinguished by the gas, which does not itself take fire.

Experiment 107.—Immerse a lighted taper in a jar of the gas : it is immediately extinguished. Take another jar of gas, and pour it over a lighted taper; notice that it extinguishes it : this shows the greater density of carbon dioxide. Take care that any drops of water remaining in the jar do not fall on the taper.

Several of the metals which have a great affinity for

oxygen burn in the gas with the displacement of carbon. If a piece of brilliantly burning magnesium wire is introduced in the gas, it continues to burn; the fragments of magnesium oxide falling to the bottom are found mingled with carbon. On the jar being rinsed with a few drops of hydrochloric acid, the oxide dissolves, and the carbon is readily distinguished :—

$$CO_2 \quad + \quad 2Mg \quad = \quad 2MgO \quad + \quad C.$$
Carbon dioxide.   Magnesium.   Magnesium oxide.   Carbon.
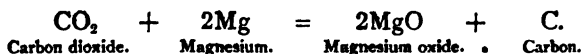
The same reaction is also effected by potassium, potassium oxide being formed instead of that of magnesium.

Experiment 108.—Fill a 4-oz. *dry* flask, by downward displacement, with carbon dioxide gas. Introduce a pellet of potassium, about the size of a pea, and heat gently until the potassium glows. When all action is over, let the flask cool, and dissolve out its contents with water ; observe that there is a residue of free carbon.

110. Carbonic Acid and Carbonates.—Carbon dioxide possesses feebly acid properties when combined with water, and therefore is sometimes called carbonic anhydride.

Experiment 109.—Pour a little litmus solution into a jar of the gas, and shake up ; the colour is changed to a port-wine tint, very different from that produced by the stronger acids.

The solution of carbon dioxide in water is undoubtedly a true acid.

$$CO_2 \quad + \quad H_2O \quad = \quad H_2CO_3.$$
Carbon dioxide.   Water.   Carbonic acid.

It is, however, very unstable, and has never been separated from an excess of water. The gas is expelled entirely by boiling the water or by freezing it.

Being a dibasic acid it forms a double series of salts, one of which is normal, the other acid. Thus we have sodium carbonate, Na_2CO_3, and sodium bicarbonate, or acid carbonate of sodium, $NaHCO_3$.

The attraction of carbon dioxide for bases has been already utilized by the student in his tests for that gas by lime-water. Lime absorbs carbon dioxide slowly from the atmosphere ; hence pieces of old mortar invariably contain it. It aids in " setting " the mortar, which becomes harder with age.

Experiment 110.—Place some fragments of old mortar in a test-tube ; pour on them some hydrochloric acid ; notice the effervescence ; when over, pour the gas into another test-tube containing lime-water ; it is rendered milky.

This experiment is not, however, absolutely conclusive, as even new lime is never so thoroughly "burned " as to entirely decompose the carbonate.

The carbonates are an important series of salts ; with the exception of those of the alkalies, they are insoluble in water. They are readily decomposed by almost any acid, with the liberation of carbon dioxide.

111. Determination of Carbon Dioxide.—The ready liberation of carbon dioxide from carbonates by the action of acids, affords a ready and comparatively simple means of determining by direct weighing the amount of that gas in a carbonate. A number of forms of apparatus have been devised for that purpose, but one of the most convenient is that known as " Schroedter's," which has been already described in the directions for the determination of the quantity by weight of hydrogen displaced by magnesium and zinc (see Chapter IX., Exp. 87, and Fig. 39). The general method of using for carbon dioxide estimations is precisely the same as there described.

Experiment 111.—Clean the Schroedter apparatus, charge the drying tube *h* (Fig. 39) with concentrated sulphuric acid, and the reservoir *d* with dilute sulphuric acid—1 of acid to 2 of water. Introduce 10 c.c. of water in the flask part *a*. Meantime take some pure anhydrous sodium carbonate, and heat a quantity of about 5 grams in a crucible over a Bunsen

flame, so as to drive off all traces of moisture. Place a watch-glass on the pan of the balance, and weigh it accurately; then add to the weights 1·06 gram, and weigh off that quantity of the sodium carbonate. At the end, take a little off, or add a little with the point of a fine penknife, until the exact weight is obtained. Then introduce a *dry* wide-stemmed funnel in *b* of the Schroedter, and pour in the 1·06 gram of carbonate, taking care that none whatever is lost. To do this, it is a good plan to fix the apparatus obliquely in a stand fitted with a clamp, so that the tubulure *b* is upright. Brush the whole of the carbonate out of the watch-glass with a dry clean camel-hair brush, and finally brush out the funnel also into the apparatus. Replace the stopper, and weigh the whole apparatus. Run in the acid carefully, so as to maintain a steady current of evolved carbon dioxide gas. As carbon dioxide is soluble in water, it is necessary at the close to heat the apparatus in order to drive off the gas dissolved in the water in *a*. For this purpose, place a clean iron plate on a tripod-stand, and heat with a Bunsen. Stand the apparatus on the top of the hot plate. Watch the liquid; as it grows hot fine bubbles of gas escape. Continue gentle heating until the evolution of gas ceases. The apparatus may be allowed to get so hot as just not to be borne by the hand, but the liquid it contains must on no account be permitted to boil. While still hot, attach a piece of indiarubber tubing to the perforated stopper *i*, and draw air through until the carbon dioxide is removed. As carbon dioxide has a distinct taste, this affords considerable guidance in determining when the whole of that gas is removed. Next allow the apparatus to become perfectly cold, and weigh. Again draw air through and weigh; continue this so long as there is any loss of weight. Take the lowest weight as the most correct. Greater accuracy may be obtained by aspirating *dried* instead of ordinary air through the apparatus, as directed in the description of hydrogen determination (Exp. 87).

Proceed, in the next place, to make a similar determination on pure calcium carbonate, for which purpose take some fragments of crystallized calcite (Iceland spar), dry in the hot-water oven, and weigh off exactly 1·00 gram. In charging the Schroedter apparatus, employ dilute nitric acid, 1 of acid to 1 of water, instead of sulphuric acid, for filling *d*, the reason being that calcium sulphate is only very slightly soluble in

water. In other respects, proceed with the determination precisely as before. It is not necessary to reduce the carbonate to powder before introducing it into the apparatus, as small fragments lend themselves to a steady and manageable current of gas.

The method of procedure may be illustrated by the record of an experiment.

Weight of watch-glass . . . 4·76 grams.
    „   sodium carbonate . . . 1·06 „
    „   glass and carbonate . . 5·82 „

Weight of Schroedter apparatus, before . 57·83 grams.
    „   „   „   after . 57·38 „
    „   evolved carbon dioxide . . 0·45 „

On calculating the molecular weight of sodium carbonate from the formula, it will be found to be 106, and in the experiment, we have taken 106 centigrams (1·06 grams), and have 45 centigrams of gas evolved. This determination affords practical proof of the fact that the action of sulphuric acid in sodium carbonate is represented by the following equation :—

$$Na_2CO_3 + H_2SO_4 = CO_2 + H_2O + Na_2SO_4$$

Molecular weight 106   44
      Taken 106   Found 45
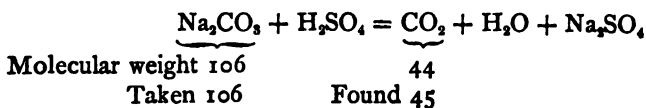
Similarly in the case of calcium carbonate, the molecular weight, 100, has been taken, and the evolved gas should also weigh as nearly as possible 44 c.g.

112. Solubility of Bicarbonates.—Several of the bicarbonates are soluble, the corresponding carbonates being insoluble. That of lime is an interesting and important example.

Experiment 112.—Boil some *hard* water from springs in chalk or limestone formations (if obtainable) in a small flask or

beaker for about a quarter of an hour ; at the expiration of that time, notice that the water has become slightly turbid by the separation of calcium carbonate.

The bicarbonate has been decomposed by heat, the carbon dioxide evolved, and the insoluble carbonate precipitated :—

$$CaH_2(CO_3)_2 \quad = \quad CaCO_3 \quad + \quad H_2O \quad + \quad CO_2.$$

Calcium bicarbonate.　　Calcium carbonate.　　Water.　　Carbon dioxide.

The same experiment may be tried in another manner, in which the formation of the bicarbonate may also be noticed.

Experiment 113.—Fit to the carbon dioxide apparatus a small wash-bottle with water ; pass the washed gas for some minutes into some lime-water in a beaker ; a precipitate at first forms, and is after a while redissolved. Then boil for some minutes ; calcium carbonate is again deposited.

113. Hard and Soft Waters.—In the preceding paragraph reference has been made to " hard water ; " the inference may be drawn that hardness is in some way connected with the presence of calcium salts in solution. It may be well to explain here what is understood by the terms " hard " and " soft " when applied to water, and to what these properties are due. Certain kinds of water, when mixed with a very small quantity of soap, immediately produce a lather, and the water acquires that peculiar feel to the hands known as " soapiness." Such water is termed " soft." Other waters when used with soap for washing purposes do not lather at all readily, and do not cause " soapiness " until a considerable quantity of soap has been consumed. When a lather is actually formed, there will be found, on examination, a layer of scum on the surface of the water. Such water is termed " hard."

Without going into the details of the composition of soap and its reaction with water when used for washing, it may be explained that soluble salts of calcium and

magnesium decompose soap, forming a precipitate which constitutes the previously mentioned scum found when washing with hard water. Consequently, if water containing calcium salts in solution is employed for washing, sufficient soap must first be added to precipitate these salts before any is available for cleansing; hence hard waters are neither so agreeable nor so economical for washing purposes.

The principal calcium and magnesium salts found in water are the carbonate and the sulphate. As seen from a previous experiment, the carbonates may be precipitated by the act of boiling, and any hardness due to their presence may be thus remedied. Consequently any hardness produced by carbonates of calcium or magnesium is termed "temporary" hardness, because such hardness is removed by boiling.

The sulphates and chlorides of calcium and magnesium are not precipitated by boiling, as their solution is caused by the water itself, and not by water plus carbon dioxide gas. Therefore hardness due to the presence of sulphates (or chlorides) of calcium or magnesium is termed "permanent" hardness.

The hardness of most waters is partly temporary and partly permanent; the two together constitute the total hardness of the water.

The hardness of water is usually tested by taking a measured quantity of the water and adding thereto in a stoppered bottle a solution in alcohol of soap of a known strength. This is introduced in small quantities at a time from a measuring instrument, the water being well shaken after each addition. As soon as a lather is thus produced which stands unbroken for five minutes, the quantity of soap solution which has been used is read off; from these data the total hardness is determined. A sample of the water is next boiled until the carbonates are precipitated; then after certain precautions the hardness is again deter-

mined with the soap solution. This gives the permanent hardness; the difference between the total and the per-manent is the temporary hardness.

114. Processes of Softening Water.—Water may be softened to the extent of the removal of the temporary hardness by the act of boiling for some minutes. Potassium and sodium carbonates precipitate calcium and magnesium salts, and themselves possess detergent or washing proper-ties; therefore these salts will remove all hardness, whether temporary or permanent. One of the characteristics of potassium and sodium carbonates is the power they possess of imparting a soapy feel to pure water. Ordinary washing soda, or soda-crystal, is commercial sodium carbonate.

115. Clark's Water-softening Process.—A most interesting process for the softening of water is that bearing the name of Clark's Process. The process depends on two chemical reactions with which the student is already familiar. First, that calcium carbonate is no longer soluble in water from which the carbon dioxide gas has been removed; secondly, that lime forms an insoluble compound with carbon dioxide gas. To soften water by Clark's Process, lime-water is added in sufficient quantity to exactly combine with the dissolved carbon dioxide gas. The whole of the lime, both that originally present in the water as carbonate and that added as hydrate, is precipitated, and the temporary hardness of the water is thus removed. The chemical reaction is represented in the following equations :—

$$\begin{cases} CaCO_3 & = & CaCO_3 \\ H_2O,CO_2 \end{cases} + CaH_2O_2 = CaCO_3 + 2H_2O.$$

Solution of carbon dioxide in water (carbonic acid), holding calcium carbonate in solution.	Lime water (calcium hydrate).	Original calcium carbonate, and also that formed from dissolved carbon dioxide and added calcium hydrate. Both insoluble.	Water.
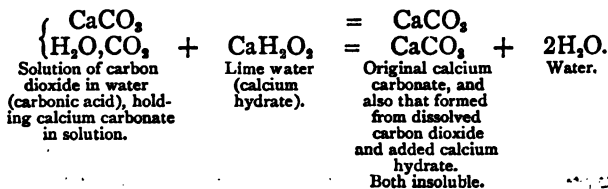
The precipitated lime is removed either by allowing it to subside or by filtration.

Experiment 114.—Procure some standard soap solution, such as is used for water analysis. (This may be prepared in the laboratory, according to directions given in works on analysis, or may be purchased from dealers in chemicals.) The following apparatus will be required : a burette, holding 50 c.c., and stand ; also a pipette, holding 50 c.c., and a stoppered bottle, of about 10 oz. capacity.

Having cleaned the various apparatus, place the lower end of the pipette in some hard water, and suck it up above the level of the graduated mark round the stem. Place the thumb on the top, and let the water drop slowly from the bottom until the graduation mark is exactly reached. Then, by removing the thumb, allow the whole of the contents of the pipette to drain into the bottle. Rinse the burette with a few drops of the soap solution, and then fill it above the zero mark at the top. Press the buttons of the spring clip, and allow the solution to run out until the zero line is reached. Next run the soap solution into the hard water in the bottle in quantities of about 1 c.c. at a time, shaking vigorously between each addition, and noticing whether or not any signs appear of a permanent lathes being formed. Continue this until, when the bottle is shaken and laid on its side, the lather does not break for five minutes. Make a note of the quantity of soap solution which has been used.

Next take a light flask of about 250 c.c. capacity ; place it on a balance, and fill with the water until the water and flask together weigh exactly 200 grams. Set the flask over a Bunsen, and boil the water for half an hour. At the end of that time place the flask again on the balance, and make up to the weight of 200 grams by adding recently boiled distilled water. This is done in order to replace the water lost by evaporation. Filter off the precipitated calcium carbonate, let the water cool, and determine the hardness in 50 c.c. precisely as before. The hardness now found is the permanent ; that which has disappeared through boiling is the temporary.

To another portion of the hard water add sodium carbonate (washing soda) until the water feels soapy to the touch ; then

test with soap solution, and notice that a lather is produced by the addition of the first few drops.

Prepare a solution of phenol-phthalein by dissolving 1 gram of the substance in 30 c.c. of strong alcohol. Take a litre of the hard water; add a few drops of the phenol-phthalein solution, and then pour in lime-water until the water acquires a faint pink tint. From 80 to 100 c.c. of lime-water will probably be required. (The object of the phenol-phthalein is to show the point when a sufficient quantity of lime has been added, as the slightest excess causes, in the presence of this substance, a red coloration.) The pink tint may be again discharged by the cautious addition of a little more of the water until the colour just disappears. Let the water stand for a few hours, and a precipitate of calcium carbonate falls to the bottom. Determine the hardness of the clear water; it should closely agree with that softened by boiling.

In softening water on the large scale, the testing with phenol-phthalein is performed, not on the whole bulk, but on small quantities taken out from time to time for the purpose of making the test.

Carbon dioxide is injurious when present in air in large quantity; all rooms should therefore have ample means of ventilation. Nine sleeping-rooms out of ten are insufficiently furnished in this respect; a room should never be used for sleeping purposes without at least the register of the stove open.

116. Composition.—Carbon dioxide contains its own volume of oxygen; consequently carbon may be burned in that gas without its undergoing any change of volume. Its composition by weight is ascertained by burning a weighed amount of carbon in excess of oxygen, and collecting and weighing the resulting carbon dioxide.

Carbon Monoxide. — Formula, CO. **Molecular weight, 27·93. Density, 13·96. Specific gravity, 0·967.**

Graphic formula, $C{=}O$.

117. **Occurrence.**—Every one is familiar with the appearance of a coke or charcoal fire, or of a coal fire which has burned perfectly clear and smokeless; the whole mass glows with a bright red heat, and hovering over the top are lambent blue flames. The origin of these may be traced in this way : in the lower parts of the grate, where air enters the fire, carbon dioxide is formed according to the following equation :—   '

$$\underset{\text{Carbon.}}{C} \quad + \quad \underset{\text{Oxygen.}}{O_2} \quad = \quad \underset{\text{Carbon dioxide.}}{CO_2.}$$

This makes its way upwards through the red-hot carbon and becomes changed by reduction to carbon monoxide, and thus an inflammable gas is produced. The same effect is produced in the following manner :—

Experiment 115.—Loosely fill an iron tube with fragments of charcoal ; fit to each end corks with pieces of quill tube passed through ; place it in a furnace and raise to a red-heat. Pass a slow current of carbon dioxide through the tube : light the gas as it emerges ; it burns with the same blue flame as is seen playing over the coke or charcoal fire.

Evidently, then, the gas is changed; for carbon dioxide is non-inflammable. The change is thus represented :—

$$\underset{\text{Carbon dioxide.}}{CO_2} \quad + \quad \underset{\text{Carbon.}}{C} \quad = \quad \underset{\text{Carbon monoxide.}}{2CO.}$$

When carbon is burned without a sufficient supply of air, carbon monoxide is formed as one of the products of combustion. This gas may also be produced by the in-complete combustion of carbon compounds.

118. **Preparation.**—In addition to the reaction just described, carbon monoxide may be prepared by heating within an iron tube a mixture of chalk (calcium carbonate) and charcoal. The chalk is decomposed into calcium oxide and carbon dioxide, which latter is converted by the char coal into the monoxide.

A mixture of carbon monoxide and free hydrogen is

produced in abundance by passing steam over or through charcoal heated to bright redness—

$$\underset{\text{Carbon.}}{C} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Hydrogen.}}{H_2}$$
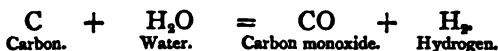
For laboratory purposes the gas is most conveniently prepared by heating certain organic compounds with concentrated sulphuric acid. This body has a very great attraction for water, in virtue of which it decomposes many substances containing hydrogen and oxygen, and assimilates the water; the remaining atoms rearrange themselves into whatever other compounds are possible. Oxalic acid, when thus treated, is split up into water, carbon dioxide, and carbon monoxide :—

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon monoxide.}}{CO.}$$

Equal volumes of carbon monoxide and dioxide are thus produced. Pure carbon monoxide may be obtained by passing the evolved gas through one or more wash-bottles containing a concentrated solution of caustic potash, by which all carbon dioxide may be absorbed, with the formation of potassium carbonate.

Experiment 116.—Place in an 8-oz. flask, fitted with either thistle funnel and leading tube, or with a leading tube only, half an ounce of oxalic acid (crystallized), and 1 oz. of concentrated sulphuric acid. Gently heat the mixture, and after the expulsion of air fill three jars with the gas over water in the pneumatic trough. As this gas is very poisonous, it should be prepared in the stink cupboard.
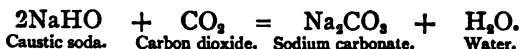
Experiment 117.—Place a light to one jar; notice that the gas burns with a blue flame.

Experiment 118.—Add some lime-water to a second, and observe that, on being shaken, it becomes milky.

Experiment 119.—Prepare a solution of crude caustic soda, and pour it into a beaker sufficiently large to hold a jar and the glass plate. Invert a third jar in this solution; hold the glass plate to the bottom of the beaker with a glass rod, and thus

remove it from the mouth of the jar. Let it stand in the soda for some time ; the liquid slowly rises, through the absorption of the carbon dioxide, until the jar is half filled. The quantity of soda solution to be taken should be roughly estimated from the size of the jar.
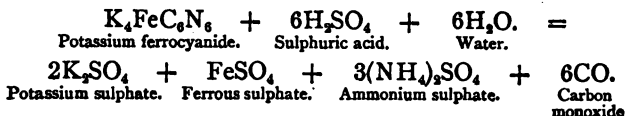
In this last experiment the soda and carbon dioxide unite and produce sodium carbonate—

$$\underset{\text{Caustic soda.}}{2NaHO} \quad + \quad \underset{\text{Carbon dioxide.}}{CO_2} \quad = \quad \underset{\text{Sodium carbonate.}}{Na_2CO_3} \quad + \quad \underset{\text{Water.}}{H_2O.}$$

Formic acid, on being similarly heated with concentrated sulphuric acid, yields pure carbon monoxide, according to the following equation :—

$$\underset{\text{Formic acid.}}{HCHO_2} \quad = \quad \underset{\text{Water.}}{H_2O} \quad + \quad \underset{\text{Carbon monoxide.}}{CO.}$$

Another method is to heat potassium ferrocyanide (yellow prussiate of potash) with sulphuric acid; the change occurring is complicated—

$$\underset{\text{Potassium ferrocyanide.}}{K_4FeC_6N_6} \quad + \quad \underset{\text{Sulphuric acid.}}{6H_2SO_4} \quad + \quad \underset{\text{Water.}}{6H_2O.} \quad =$$

$$\underset{\text{Potassium sulphate.}}{2K_2SO_4} \quad + \quad \underset{\text{Ferrous sulphate.}}{FeSO_4} \quad + \quad \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} \quad + \quad \underset{\substack{\text{Carbon}\\\text{monoxide}}}{6CO.}$$

When the monoxide is required in a state of absolute purity, the former of these two reactions is the preferable. The latter yields the gas in large quantities, but usually accompanied by traces of carbon dioxide as an impurity.

Experiment 120.—Take a 16, or preferably a 32, oz. flask, fitted with thistle funnel and leading tube. Insert, in lumps, a quarter of an ounce of commercial ferrocyanide and about 2 oz. of sulphuric acid. Get three jars ready filled with water. and inverted in the pneumatic trough. Fix the flask in the retort-stand with the end of the leading tube in the trough ; apply heat carefully. As soon as the gas begins to be evolved, remove the flame, as the action continues with extreme rapidity. When the whole of the air is expelled, fill the three jars with gas. The end of the thistle funnel should be pushed down as

near as possible to the bottom of the flask without touching. Sometimes, through lack of sufficient precautions, the gas is produced so violently that the pressure forces the boiling acid up through the funnel. Should this be the case, remove the light, take the delivery tube out of the water, and stand out of the reach of splashes of falling acid. Throw whiting on any which is spilled on the working bench, and then wipe off with an old duster.

119. Properties.—Carbon monoxide is a colourless gas; it has a slight oppressive odour, and is extremely poisonous, producing a painful headache even when present in small quantities in air. It is but slightly soluble in water: 100 volumes dissolve 2·434 volumes of the gas at 15° C. It liquefies only under very great cold and pressure. Carbon monoxide is inflammable and a non-supporter of combustion; when burned, its own volume of carbon dioxide is produced, half of its volume of oxygen being required—

$$\underset{\text{Carbon monoxide.}}{2CO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{2CO_2}$$

Experiment 121.—Immerse a lighted taper in a jar of the gas; it is extinguished, but the gas burns with a blue flame, as when made from oxalic acid.

This gas is devoid of acid properties, and consequently. is without action on lime-water.

Experiment 122.—Add some lime-water to a jar of the gas and shake up; no turbidity is produced. Inflame the gas, replace the plate, and then again shake; the lime - water becomes milky through the presence of carbon dioxide.
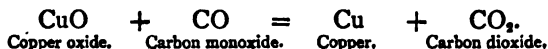
Carbon monoxide acts as a powerful reducing agent, and is frequently used in metallurgical operations for the production of metals from their oxides.

Experiment 123.—Arrange a piece of combustion tubing about 18 inches in length in the combustion furnace, and connect, by means of a cork, piece of quill tubing, and indiarubber tube, with an apparatus evolving carbon monoxide gas. (The

most convenient method of obtaining the gas for this purpose is from oxalic and sulphuric acids. The gas may be passed through a wash-bottle containing caustic soda, but the carbon dioxide takes no part in the reaction.) Partly fill the combustion tube with granulated copper oxide, expel the air by passing a slow current of carbon monoxide, and then light the furnace. On the tube becoming red-hot, notice that the oxide is reduced to the metallic state.

If wished, carbon monoxide, free from the dioxide, may be prepared and used for this experiment; and the gas, after its passage through the red-hot copper oxide, passed into lime-water. The precipitate of calcium carbonate shows the production of carbon dioxide from the reaction of the monoxide and copper oxide on each other.

The following equation shows the chemical change which occurs during this experiment :—

$$\underset{\text{Copper oxide.}}{CuO} \quad + \quad \underset{\text{Carbon monoxide.}}{CO} \quad = \quad \underset{\text{Copper.}}{Cu} \quad + \quad \underset{\text{Carbon dioxide.}}{CO_2}.$$

120. Composition.—The composition of carbon monoxide is determined by explosion with excess of oxygen in the eudiometer; the volumes of the monoxide and of the oxygen are observed. After the explosion potassium hydrate is introduced; the diminution in volume represents the carbon dioxide formed, which is absorbed. From these data the composition of the monoxide is readily deduced.

Summary.

There are two oxides of carbon—carbon monoxide and dioxide.

Carbon dioxide occurs in the atmosphere and in combination with lime in limestone; may be prepared by heating limestone, or more conveniently by the action of an acid, as hydrochloric. It is a colourless gas, with a very faint odour and taste; may be condensed by pressure; is soluble in water; is half as heavy again as air; hence may be poured from vessel to vessel; remains for a long time in the bottom of brewers' vats, etc.; is non-inflammable and a non-supporter of combustion of most

substances, but allows certain metals, as potassium and magnesium, to burn in it. The solution of the gas is slightly acid to litmus ; it forms a series of important salts, which are readily decomposed by a stronger acid. By means of this reaction the weight of carbon dioxide in a carbonate can be determined analytically. All the carbonates are insoluble in water except those of the alkalies ; certain others form soluble bicarbonates with excess of carbon dioxide : lime exists in this form in most hard waters. Carbon dioxide contains its own volume of oxygen.

Carbon monoxide is formed in the burning of coke by the deoxidation of carbon dioxide ; the same change occurs if carbon dioxide is passed over red-hot charcoal in an iron tube. The gas is more generally prepared by the action of sulphuric acid on some organic bodies, as oxalic or formic acids, or potassium ferrocyanide.

Carbon monoxide is a colourless gas with a faint oppressive odour ; is very poisonous ; slightly soluble in water. It is inflammable and a non-supporter of combustion ; it is devoid of acid properties. Carbon monoxide is a powerful reducing agent. Its composition is ascertained by explosion in the eudiometer.

OBJECT DEMONSTRATION.

Note the appearance and physical properties of oxalic and formic acids ; also of potassium ferrocyanide.

LABORATORY HINTS.

A solution of crude caustic soda is conveniently kept for use in the laboratory ; the soda is very cheap, and the same solution can be used several times for such an experiment as No. 119. The solution which has been once used should not be replaced in the same bottle.

CHAPTER XIV.

121. Hydrocarbons.—The compounds of carbon with hydrogen are known as hydrocarbons, or hydrides of carbon. These bodies are exceedingly numerous, and as most of them are distinctly of organic origin, their study is usually undertaken as a part of organic rather than inorganic chemistry. Only the following simple and important hydrocarbons will receive attention in this work :—

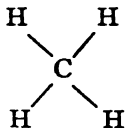|	
Marsh Gas, Light Carburetted Hydrogen, or Methyl Hydride	. CH_4.
Acetylene	. C_2H_2.
Olefiant Gas, Heavy Carburetted Hydrogen, or Ethene	. C_2H_4.

Marsh Gas, Methyl Hydride.—Formula, CH_4. Molecular weight, 15·97. Density, 7·98. Specific gravity, 0·551.

Graphic formula,

$$\begin{matrix} H & & H \\ & \diagdown \quad \diagup & \\ & C & \\ & \diagup \quad \diagdown & \\ H & & H \end{matrix}$$

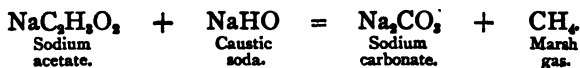**122. Occurrence.**—This gas is evolved during the decomposition of dead vegetable matter; hence is found in marshy districts, and has thus received its common name of marsh gas. On watching stagnant water, bubbles of the gas may be seen to arise, and may be collected by inverting

a gas-jar, filled with water, in the pool. During the changes which have occurred, as coal has been formed from vegetable growths, marsh gas has also been evolved, and has remained imprisoned within cavities of the coal itself. As the coal is removed by the miner the gas escapes from these cavities into the mine, and, mixing with the air, forms the explosive mixture which has been the cause of so many terrible colliery accidents. The collier knows this gas as "fire-damp."

123. Preparation.—Marsh gas may be prepared by heating together a mixture of sodium acetate and caustic soda, when the following reaction occurs :—

$$NaC_2H_3O_2 \quad + \quad NaHO \quad = \quad Na_2CO_3 \quad + \quad CH_4$$

$NaC_2H_3O_2$	$NaHO$	Na_2CO_3	CH_4
Sodium acetate.	Caustic soda.	Sodium carbonate.	Marsh gas.

Experiment 124.—Arrange an iron tube closed at one end (a piece of inch gas-barrel) as a retort for the production of gas; fitting a cork and delivery tube to the end remaining open. Introduce into this a mixture of two parts of sodium acetate with one of caustic soda. Apply heat, and collect three jars of the evolved gas.

124. Properties.—Marsh gas is a light colourless gas, and has consequently received the name of light carburetted hydrogen. It is not a supporter of combustion, but burns with a non-luminous flame, something like that of hydrogen, but slightly tinged with yellow. Mixtures of either air or oxygen with this gas explode violently on ignition.

Experiment 125.—Apply a light to one of the jars of gas already prepared; notice the nature of the flame. When the combination is over, add some lime-water and shake up; the lime-water turns milky. Notice also that a film of moisture is deposited on the sides of the jar. Mix in a stout explosion-tube one volume of marsh gas with two volumes of oxygen, and apply a light; the mixture explodes. Repeat the experiment with a mixture of one volume of the gas with ten of air. Test the gas remaining in the bottle with lime-water for carbon

dioxide. Pour the gas upwards from one jar into another and set light; in this way observe that, like hydrogen, it is much lighter than air.

The carbon dioxide and nitrogen remaining after the combustion or explosion of marsh gas and air are known by the miner as "choke-" or "after-damp."

Until recently, marsh gas was viewed as a permanent gas, but, in common with hydrogen and other gases, has now been liquefied.

125. Composition by Volume.—The composition of this gas may be ascertained by explosion with excess of oxygen in the eudiometer. If ten volumes of marsh gas be mixed with twenty-five volumes of oxygen, there will be found after explosion, at a temperature above 100° C., thirty-five volumes of gas. On cooling to normal temperature the volume of gas contracts to fifteen; there must therefore have been present twenty volumes of water vapour. On introducing caustic potash a further absorption of ten volumes occurs, showing that ten volumes of carbon dioxide have been formed. The residual five volumes of gas are found on examination to be oxygen. One volume, therefore, of this gas requires for its combustion two volumes of oxygen, and produces one volume of carbon dioxide and two of water vapour.

Remembering that by Avogadro's law the molecular volume of all gases is alike, and that the molecule of hydrogen contains two atoms, then as two volumes of the gas yield two volumes of carbon dioxide, or one molecule yields a molecule of carbon dioxide, one molecule of marsh gas contains one atom of carbon. Again, the two volumes of marsh gas produce four volumes of water vapour, that is, one molecule of marsh gas yields two molecules of water; and as each molecule of water contains two atoms of hydrogen, the molecule of marsh gas contains four atoms of hydrogen, the formula must consequently be CH_4.

126. Composition by Weight.—The composition by weight is ascertained by passing a known volume of marsh gas through a combustion tube containing red-hot copper oxide. Carbon dioxide and water are formed, and are absorbed in weighed tubes containing respectively calcium chloride, which absorbs the water, and caustic potash, by which the carbon dioxide is retained. The increase in weight gives the amounts of these two bodies formed from the marsh gas. In an experiment a volume of CH_4, equivalent to 1000 c.c. at N.T.P., was passed over red-hot copper oxide; there were produced 1·611 gram of water and 1·965 gram of CO_2. From these data the composition of the gas is thus calculated :—

Weight of 1000 c.c. = 0·0896 × 7·98 (density) = 0·715 gram.

Weight of carbon $= \dfrac{1·965 \times 12}{44} = 0·536$ gram.

Weight of hydrogen $= \dfrac{1·611 \times 2}{18} = 0·179$ gram.

From these numbers the percentage composition may be calculated in the manner already explained.

The simplest possible formula may be determined thus :—

$\left. \begin{array}{l} \dfrac{0·536}{12} = 0·044 \\[2mm] \dfrac{0·179}{1} = 0·179 \end{array} \right\}$ Numbers in ratio of the number of atoms of carbon and hydrogen.

$\left. \begin{array}{l} \dfrac{0·044}{0·044} = 1 \text{ of C} \\[2mm] \dfrac{0·179}{0·044} = 4 \text{ of H} \end{array} \right\}$ Lowest number of atoms of C and H in the molecule.

The simplest possible formula of marsh gas must be, from this experiment, CH_4. Whether or not this is the true molecular formula may be determined by calculating the density from the formula, CH_4.

$$\text{Density} = \frac{\text{molecular weight} = \text{C, } 12 + \text{H}_4, 4 = 16}{2} = 8.$$

This number agrees with the density as determined by experiment; and therefore CH_4 is the correct molecular formula.

Acetylene.—Formula, C_2H_2. Molecular weight, 25·94. Density, 12·97. Specific gravity, 0·896. Graphic formula,
$$H - C - C - H.$$
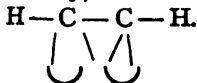
127. Occurrence.—Acetylene is produced during the combustion of many hydrocarbons in a limited supply of air. Thus, when a Bunsen burner lights at the bottom of the tube, acetylene is produced in considerable quantity.

128. Preparation.—By the direct union of carbon and hydrogen at a high temperature acetylene may be formed. The most convenient method of thus preparing the gas is by passing a current of electricity, from a powerful voltaic battery, through two electrodes of carbon enclosed in a glass flask containing hydrogen.

129. Properties.—Acetylene is a gas possessing a peculiar and disagreeable odour; it is a non-supporter of combustion, and burns with a bright and luminous flame.

130. Composition.—The composition, both by volume and by weight, of this gas may be ascertained in precisely the same manner as that of marsh gas. Acetylene consists of two atoms of carbon combined in the molecule with two of hydrogen, and therefore has the formula C_2H_2.

Ethylene, Ethene, Olefiant Gas, or Heavy Carburetted Hydrogen.—Formula, C_2H_4. Molecular weight, 27·94. Density, 13·97. Specific gravity, 0·965.

Graphic formula,
$$
\begin{array}{ccc}
H & & H \\
 & \diagdown \quad \diagup & \\
 & C = C & \\
 & \diagup \quad \diagdown & \\
H & & H
\end{array}
$$
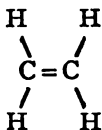
131. Occurrence.—This gas is one of the most important constituents of coal-gas, being formed when the coal is subjected to destructive distillation.

132. Preparation.—Ethylene is most readily prepared by the action of concentrated sulphuric acid on alcohol, when the acid abstracts the elements of water from the alcohol—

$$\underset{\text{Alcohol.}}{C_2H_6HO} = \underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O.}$$

Experiment 126.—Mix in a large flask, fitted with a delivery-tube, one part of alcohol with five parts of concentrated sulphuric acid, and warm gently. Ethylene is readily evolved, and may be collected in jars over water. Collect two jars of the gas.

133. Properties.—Ethylene burns readily with a bright luminous flame, evolving at the same time considerable quantities of smoke. The gas, on being mixed with air or oxygen, explodes violently.

Experiment 127.—To one of the jars of gas already prepared apply a lighted taper; notice the bright flame with which the gas burns.

Mix in an explosion-tube one volume of ethylene with three volumes of oxygen, and light; the mixture violently explodes.

. Ethylene combines directly with chlorine to form an oily liquid of the composition $C_2H_4Cl_2$—

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Ethylene dichloride.}}{C_2H_4Cl_2}$$
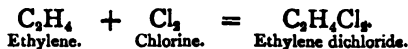
134. Composition.—The composition by volume of ethylene is determined by exploding the gas with excess of oxygen in a eudiometer. Thus if ten volumes of ethylene be taken and forty volumes of oxygen added, there will be found after explosion, the temperature being maintained above 100° C., fifty volumes of gas; that is to say, the volume remains unaltered. On cooling, the volume contracts to thirty, showing that twenty volumes of water gas

have been produced. The addition of caustic potash causes an absorption of twenty volumes, showing that that amount of carbon dioxide has been formed. The residual ten volumes of gas are found on testing to be oxygen. One volume, therefore, of ethylene produces on combustion two volumes of carbon dioxide and two volumes of water. Applying, as in the case of marsh gas, Avogadro's law, one molecule of ethylene yields two molecules of carbon dioxide and two molecules of water; therefore the molecule of ethylene must contain two atoms of carbon and four of hydrogen, and its formula must be C_2H_4.

By passing a known volume of ethylene over red-hot copper oxide, and collecting and weighing the resultant water and carbon dioxide, the composition by weight may be determined. Thus 1000 c.c. at N.T.P. having been thus treated, there will have been formed 1·609 gram of water and 3·934 gram of carbon dioxide.

$$\text{Weight of 1000 c.c.} = 0·0896 \times 13·97 \text{ (density)}$$
$$= 1·2517 \text{ gram.}$$
$$\text{Weight of carbon} = \frac{3·934 \times 12}{44} = 1·0729 \text{ gram.}$$
$$\text{Weight of hydrogen} = \frac{1·6092 \times 2}{18} = 0·1788 \text{ gram.}$$

The percentage composition may be readily calculated from these numbers.

The simplest formula may be thus deduced :—

$$\left. \begin{array}{l} \dfrac{1·0729}{12} = 0·0894 \\[2mm] \dfrac{0·1788}{1} = 0·1788 \end{array} \right\}$$ Numbers in ratio of the number of atoms of carbon and hydrogen.

$$\left. \begin{array}{l} \dfrac{0·0894}{0·0894} = 1 \text{ of C} \\[2mm] \dfrac{0·1788}{0·0894} = 2 \text{ of H} \end{array} \right\}$$ Lowest number of atoms of C and H in the molecule.
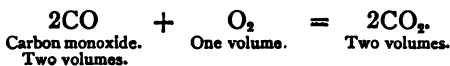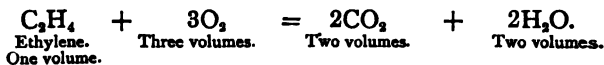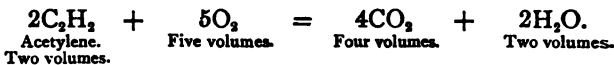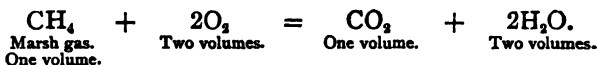
The simplest possible formula is therefore CH_2;

Whether or not this is the true molecular formula may be determined by calculating the density according to this formula :—

$$\text{Density} = \frac{\text{molecular weight} = C, \ 12 + H_2, \ 2 = 14}{2} = 7.$$

But the density as determined by direct experiment is 14; therefore the molecular formula must be just double CH_2, that is to say, the molecule is represented by C_2H_4.

135. Combustion of Marsh Gas, Acetylene, and Ethylene.—The combustion of these three bodies affords some interesting examples of the laws of combination by volume. Subjoined are the molecular equations representing the reactions which occur, together with those of some other examples of combustion already familiar to the student.

$$CH_4 \quad + \quad 2O_2 \quad = \quad CO_2 \quad + \quad 2H_2O.$$
Marsh gas.   Two volumes.   One volume.   Two volumes.
One volume.

$$2C_2H_2 \quad + \quad 5O_2 \quad = \quad 4CO_2 \quad + \quad 2H_2O.$$
Acetylene.   Five volumes.   Four volumes.   Two volumes.
Two volumes.

$$C_2H_4 \quad + \quad 3O_2 \quad = \quad 2CO_2 \quad + \quad 2H_2O.$$
Ethylene.   Three volumes.   Two volumes.   Two volumes.
One volume.

$$C \quad + \quad O_2 \quad = \quad CO_2.$$
Carbon.   One volume.   One volume.

$$2CO \quad + \quad O_2 \quad = \quad 2CO_2.$$
Carbon monoxide.   One volume.   Two volumes.
Two volumes.

$$2H_2 \quad + \quad O_2 \quad = \quad 2H_2O.$$
Hydrogen.   One volume.   Two volumes.
Two volumes.

$$H_2 \quad + \quad Cl_2 \quad = \quad 2HCL$$
Hydrogen.   One volume.   Two volumes.
One volume.

These equations show very clearly the relation which exists between the volumes of gases and the respective volumes of oxygen required for their combustion. They afford additional illustrations of the method of deducing these quantities from the molecular equations. **As gaseous**

molecules are assumed (at the same temperature and pressure) to occupy the same space, it follows that the number of molecules of any gas participating in a chemical change represents the number of volumes of the gas concerned.

136. Nature of Combustion.—Every one is familiar with the general idea of combustion as an act of burning. We may now inquire a little more closely into what is understood by this term. It has already been incidentally remarked that heat is produced when combination occurs between two substances; for instance, the addition of water to sulphuric acid causes a considerable elevation of temperature, because the water and acid unite with each other. There are many other cases in which the heat evolved is much more intense, as, for example, when phosphorus combines with oxygen. Whenever the heat caused by chemical union is sufficiently intense to raise the resultant substances to a temperature at which they emit light, the act of union is termed "combustion." The term has gradually come to receive a somewhat wider application; thus certain processes of decay, and also the chemical changes which produce animal heat, are cases of combination with oxygen. Such chemical actions are frequently termed instances of "slow" combustion.

137. Inflammable Bodies and Supporters of Combustion.—The substances participating in the act of combustion are classified into inflammable bodies on the one hand, and supporters of combustion on the other. Thus, when hydrogen burns in oxygen, the hydrogen is said to be inflammable, and the oxygen a supporter of combustion. The terms "combustible" and "supporters of combustion" are, however, purely relative. We happen to live in an atmosphere of which oxygen is the active ingredient; when a jet of hydrogen is burned, what takes place is that at the orifice of the jet the hydrogen and the oxygen come in

contact, and combination ensues. If the atmosphere consisted of hydrogen, then that element would be classified as a supporter of combustion, and oxygen and similar bodies would be inflammable substances. Experiment readily demonstrates that oxygen burns in an atmosphere of hydrogen.

Experiment 128.—Fill a large globe, such as is used for the combustion of phosphorus in oxygen, with hydrogen gas : arrange the globe with its mouth downwards in a retort- or other stand, covering the mouth with a glass plate. Fill a bladder or small gas-bag with oxygen, and attach to it by india-rubber tubing a piece of glass tube, with the end drawn out into a jet. Place a weight on this bag, and so arrange it as to produce a gentle stream of oxygen from the jet. Light the hydrogen at the mouth of the globe, and steadily introduce the jet of oxygen. The oxygen will be ignited at the flame of the burning hydrogen, and as it is pushed up into the globe will continue to burn, showing clearly that oxygen burns in an atmosphere of hydrogen. The same experiment may be performed with coal-gas and air.

It is seen, therefore, that for combustion to occur, contact of the two substances is necessary. It is a matter of indifference which of the two envelops the other. But oxygen being so widely distributed, and the essential constituent of the atmosphere, it and like bodies are classified as supporters of combustion ; while hydrogen and bodies of similar character are termed inflammable.

138. Explosion.—When two substances, the one inflammable and the other a supporter of combustion, are intimately mixed with each other, on ignition combination occurs with extreme rapidity. The heat developed enormously increases the pressure of the gases produced as a result of the chemical action, and these give the surrounding air such a severe shock as to cause a loud detonation. Extremely rapid combustion, attended with more or less noise, is termed explosion. The mixture which thus

explodes is termed an explosive body. If explosive mixtures be confined and then exploded, the resultant pressure may shatter the containing vessel. The explosive force of gunpowder is thus utilized for destroying large masses of rock. A hole is bored in the rock, filled with the powder, and then ignited, with the result of shattering the rock into fragments. The great pressure exerted by exploding gunpowder is employed in guns for the purpose of propelling the bullet. Another interesting example of explosive force being utilized is that of the gas engine, in the cylinder of which a mixture of gas and air is caused to explode. The piston is driven forward by the force of the explosion.

139. Heat of Combustion.—Not only do substances in burning give out heat, but **the amount of heat evolved by the combustion (combination with oxygen) of a given weight of any substance is always the same.** Thus, whether the substance be burned slowly or rapidly, provided it is burned to the same products of combustion, the total amount of heat generated never varies. The following table gives the number of heat units evolved by the combustion respectively in oxygen and chlorine of one gram of each substance. The student is reminded that a heat unit is the quantity of heat necessary to raise one gram of water from 0° to 1° C.

HEAT DEVELOPED DURING COMBUSTION.

Substance.	In oxygen. Heat units.	In chlorine. Heat units.
Hydrogen . . .	34,462	24,087
Carbon . . .	8,080	
Sulphur . . .	2,220	
Phosphorus . .	5,747	3,422 (?)
Carbon monoxide .	2,634	
Marsh gas . .	13,063	
Olefiant gas . .	11,942	
Alcohol . . .	6,909	

Of the elements hydrogen develops by far the greatest amount of heat on combustion, the next place being taken by carbon. Of the various compounds of carbon it will be observed that carbon monoxide, during its further combustion to the dioxide, evolves a considerable quantity of heat. It will be of interest to compare the amount of heat evolved in the two stages of oxidation of carbon. As carbon monoxide contains, according to its formula, but $\frac{12}{28}$ of its weight of carbon, it is evident that one gram of carbon would yield $\frac{28}{12}$ gram of carbon monoxide, and, consequently, that one gram of carbon as monoxide would, in its further oxidation to carbon dioxide, evolve

$$\frac{2634 \times 28}{12} = 6146 \text{ heat units.}$$

But the total number of heat units evolved by the complete combustion of carbon is only 8080. Therefore one gram of carbon evolves in oxidation to the monoxide

$$8080 - 6146 = 1934 \text{ heat units,}$$

and during further oxidation to the dioxide, 6146 heat units. The student is already aware that when the carbon dioxide formed in a fire of carbon passes upwards through red-hot carbon, it is reduced to the monoxide, which in its turn burns on the upper surface of the fire, where there is free access to air. Whenever carbon is burned with a limited supply of oxygen, as where a draught of air is drawn through a furnace containing large quantities of coke or other form of carbon, the monoxide is the chief product of combustion. This cannot burn until it reaches the air, and accordingly in the older forms of furnace used in metallurgical operations, particularly the blast furnace used for the smelting of iron ores, enormous quantities of carbon monoxide were formed and allowed to burn to waste on the tops of the furnaces. The value of this gas as a fuel is now recognized, and it is consequently drawn off from the upper part of the furnaces and utilized for heating purposes.

140. Temperature of Combustion.—Although the absolute amount of heat evolved by the combustion of a unit weight of hydrogen, for example, is always the same, yet the temperature produced may vary within wide limits. Thus, first of all, if within a given space, hydrogen is caused to burn in one instance at twice the rate of another, it follows that, as a greater number of units of heat are evolved in the same period of time, the temperature of that space will be raised proportionately higher. There are other causes which influence the temperature produced by combustion ; for example, a jet of hydrogen, which burns the same number of cubic feet per hour, produces a flame of much higher temperature when it burns in oxygen than it does when burning in air. If 2 grams of hydrogen are burned in oxygen, the heat evolved has to raise the temperature of the 18 grams of water produced. But if the oxygen is obtained from air, then not only have there to be heated the 16 grams of oxygen in the water produced, but also the 53·5 grams of nitrogen with which it, the oxygen, was mixed. The same number of units of heat are in the one case spread over 18 grams ; in the other, over $18 + 53·5 = 71·5$ grams of gaseous matter : it follows that the temperature in the first instance must be very much higher than in the second.

141. Oxyhydrogen Blowpipe.—This instrument is a contrivance for utilizing to the fullest extent the heating power of a flame of hydrogen fed with oxygen. The blowpipe consists of a platinum jet, leading from a small chamber, into which enters two pipes connected with gas-bags or other vessels containing respectively hydrogen and oxygen under pressure. By means of a tap, hydrogen is first turned on and then lighted. In the next place the oxygen tap is also gradually opened, and there emerges from the jet a mixture of hydrogen and oxygen ; the flame becomes smaller, and is scarcely more luminous than the ordinary flame of hydrogen itself. By means of this blowpipe,

platinum and other most refractory substances may be reduced to the liquid state.

142. Luminosity of Flame.—The student will probably think it strange that, although the temperature of the flame of hydrogen burning in oxygen is the highest due to combustion, yet the flame is almost absolutely devoid of luminosity. The reason is that gases—and especially those of low density—radiate very little light even when intensely hot, while solids at a much lower temperature emit light most abundantly. This is strikingly illustrated by inserting some solid substance in the oxyhydrogen flame; if the flame from the oxyhydrogen blowpipe is caused to impinge on a piece of lime, the light emitted is one of the most intense known, and constitutes the well-known lime-light. It is here the solid substance which radiates so much light, although its temperature must be lower than that of the oxyhydrogen flame by which it is heated.

The various inflammable hydrocarbons burn with different degrees of luminosity; marsh gas and alcohol emit but very little light; olefiant gas, on the other hand, burns with a very luminous and smoky flame. As a general rule, the heavier hydrocarbons produce more light in burning than those which are less dense. During the combustion of such a body as olefiant gas, the hydrogen, being more inflammable, seizes first hold of the oxygen, and more or less of the carbon is liberated either in the free state or else as vapour of exceedingly dense hydrocarbons. The finely divided particles of carbon or dense hydrocarbons, as the case may be, are heated by the burning hydrogen, and by abundantly emitting light impart luminosity to the flame.

143. Structure of Flame.—The actual structure of a flame may be studied by observing a jet of coal gas burning from the end of a round pipe, such as A in Fig. 43. In the interior of the flame there is a jet of unburnt gas, marked *a, a* in the figure, and appearing black by contrast with the

surrounding brighter portions of the flame, by which it is enveloped. This bright or luminous zone, *f, e, g,* is that portion of the flame in which combustion of the hydrogen is proceeding, the unburnt carbon being thereby heated to the point at which it emits light. In such a burner as is figured, there will be seen ascending from the upper portion of this zone a stream of smoke, consisting of carbon, which altogether escapes combustion. Outside *f, e, g* there may be distinguished another envelope, *b, c, d,* scarcely at all luminous, and much resembling the flame of burning hydrogen. This outer zone is that in which there is an ample supply of atmospheric oxygen, and consequently complete combustion : this is the hottest part of the flame, although the absence of solid particles causes it to be almost non-luminous.

FIG. 43.—Section through flame.

The same divisions of the flame occur in a candle ; only in that case the dark interior portion consists of the solid matters of the candle, first melted, then drawn up into the heart of the flame by the capillary attraction of the wick, and finally vaporized by the heat of the flame.

144. Bunsen's Gas Burner.—When a gas flame is required for heating purposes only, it is desirable to attain the most perfect combustion possible. This end is accomplished by causing an admixture of air with the gas before it is burned. The gas burner invented by Bunsen is familiar to every chemical student. Examination shows that at the bottom of the upright tube are two or more holes communicating with the air ; on unscrewing this tube a small jet is seen within, from which the gas emerges. The air-holes may be wholly or partly closed by turning a ring which is fixed around them.

Experiment 129.—Take a Bunsen burner and examine its construction ; close the air-holes, and light the burner. Place

over it on a tripod stand a flask or other vessel containing a measured quantity of cold water; observe the length of time before it boils; notice also that the bottom of the flask becomes covered with soot.

Look at the flame, and notice that the gas is evidently escaping but slowly from the top of the burner; the flame is blown about readily by the most gentle air-currents. Holding the burner in the hand, turn it over in a horizontal position, the flame still remains vertical. Next slowly open the air-holes until the whole of the flame has acquired the pale blue tint of perfect combustion. Notice that a much more rapid current of gases emerges from the tube; the flame is very little affected by gentle air-currents. Turn the burner over into the horizontal position; the flame also lies horizontally. Take a piece of smouldering tinder and hold it near the air-holes; the smoke is drawn in, showing that a current of air is entering. All these observations go to prove that the gas draws air up with it, and that a mixture of the two burns at the top of the tube.

Again place over the burner the flask of cold water, and with the conditions the same as before, except that air is being admitted, observe the length of time necessary to cause the water to boil. The boiling-point is reached in less time, and the flame is entirely smokeless, not causing the slightest mark of soot on the flask.

145. Blowpipe Flame.—The effect of converting a luminous flame into one devoid of light, but possessing considerable heating powers, is also obtained by blowing a current of air from a jet into the flame. The instrument employed for this purpose is termed a blowpipe, and is described at length in the analytic section of this work.

146. Lamp Chimneys.—The effect of the lamp chimney of a petroleum or Argand gas lamp is apparently just the opposite of that produced by the Bunsen burner. If either of these be lighted, it burns with a dull, smoky flame, but on fixing the chimney the flame becomes smokeless and much more luminous. The first result of the action of the chimney is to draw a current of air up around the flame (in the case of the Argand through the interior as

well as the exterior). That this produces greater brightness
is at first sight contradictory to what has already been seen
of the effects of air in the Bunsen burner. But with the
lamp chimney the air is drawn up, not into the flame, but
surrounding it; the effect of this is more complete and
intense combustion in the outside zone of the flame; con-
sequently the luminous envelope is heated more intensely
and emits more light. The brisker current of air causes
also the complete consumption of the smoke. If the current
of air be too rapid, the brightness of the flame is thereby
diminished, for with excess of air the envelope of complete
combustion is unduly enlarged at the expense of that of
luminosity; the flame, in fact, partakes more or less of the
character of that of the Bunsen. That in some cases the
chimney causes too great a draught may be readily seen by
partly closing the top by placing on it a small piece of tin-
plate. This lessens the draught, and very frequently causes
the flame to increase in size and emit more light.

Summary.

The compounds of hydrogen with carbon are very numerous.
Marsh gas, acetylene, and olefiant gas are the simplest.

Marsh gas occurs as a product of decomposition of vegetable
matter; may be prepared by heating sodium acetate and caustic
soda. The gas is of low density, colourless, inflammable, non-
supporter of combustion, and produces carbon dioxide and
water on burning. Composition is determined by explosion
with oxygen in the eudiometer, and by passage over red-hot
copper oxide.

Acetylene is formed when hydrocarbons are burned with
limited supply of air, and also by direct union at high tempera-
tures of carbon and hydrogen. The gas is colourless, possesses
a peculiar odour, is inflammable, and a non-supporter of com-
bustion. Composition is determined in a similar way to that of
marsh gas.

Ethylene occurs as an important constituent of coal gas;
is prepared by heating alcohol with sulphuric acid. Possesses
a pleasant odour, is inflammable, and a non-supporter of

combustion.   Composition ascertained in a similar way to that of marsh gas.

These three gases require different volumes of oxygen for their combustion ; this is seen by studying their formulæ.

Nature of combustion, inflammable bodies, and supporters of combustion : these terms relative.   Nature of explosion, quantity of heat produced by combustion, temperature of combustion, oxyhydrogen blowpipe, luminosity of flame due to solid particles. Structure of flame, effect of air as shown in Bunsen burner and use of lamp chimneys.

OBJECT DEMONSTRATION.

If practicable, collect and note properties of marsh gas actually obtained from stagnant pool.

Note appearance and properties of alcohol, both pure and impure, as in methylated spirits.

Examine oxyhydrogen blowpipe, and observe effect on lime and on platinum wire.

Examine an Argand burner, also that of an ordinary paraffin lamp: note the effect of the chimney on the flame of each.

LABORATORY DIRECTIONS.

It is possible to use a glass flask for Experiment 124, but the heat is extremely likely to crack it.

In heating sulphuric acid and alcohol together, great care must be taken to avoid the alcohol taking fire.   The flask used should be capacious, as the mixture froths.

In Experiment 128 take care that the hydrogen and oxygen used are pure, otherwise there is a risk of explosion.

CHAPTER XV.

Nitrogen.—Symbol, N. Atomic weight, 14·01. Density, 14·01. Specific gravity, 0·971. Molecular weight, 28·02. Molecular volume, ▢▢

147. Occurrence.—Nitrogen exists in the free state in the atmosphere, in combination with oxygen and metals in certain native nitrates, and also is an essential constituent of many organic compounds.

148. Preparation.—There are several methods of preparing this gas, based on the removal of oxygen from the air by bodies having an affinity for that element; but in order that nitrogen only shall remain, it is necessary that the substance used be such that the resulting body can be easily separated from the gas. Phosphorus is very convenient for this purpose, as the solid pentoxide produced is very soluble in water.

FIG. 44.—Preparation of nitrogen from air.

Experiment 130.—Procure an upright deflagrating spoon on stand; place in it a small piece of dried phosphorus; stand the spoon in the pneumatic trough with water; ignite the phosphorus, and immediately invert over it a gas jar. At first a few bubbles of air escape, owing to their being expanded by

heat; the phosphorus soon ceases to burn; the fumes are dissolved by the water, and rather less than four-fifths of the original volume of gas remains : the loss is mostly oxygen, but there is in addition that resulting from the escape due to expansion.

A more accurate measurement may be made by removing the oxygen by the slow oxidation of phosphorus, which goes on at ordinary temperatures.

Experiment 131.—Take a piece of phosphorus about an inch long, and scrape off the oxide from it, holding it all the while under water; fix this in the spoon and proceed exactly as before, except that the phosphorus is not lighted. If only a small piece is used, the phosphorus pentoxide first formed absorbs water, and so the whole piece, if it lie below the level of the top of the spoon, may be covered and prevented from undergoing further oxidation. At the end of from two or three days to a week, observe and mark how far the water has ascended. Ascertain what proportion the whole contents of the jar bears to the gas remaining ; this is easily done by filling the jar with water, and pouring it out into the graduated measure, then in the same way measuring its contents when filled to the mark indicating the absorption of oxygen. As the combination goes on in this case without any sudden heat, there is no loss by expansion.

By experiment it is also easy to demonstrate that the phosphorus, in the act of oxidation, gains in weight.

Experiment 132.—Select a light Bohemian globular flask, about 4 inches in diameter, and fit it with a good cork. To this cork fit two tubes, as in Fig. 45. The tube *a* must be bent and reach to the bottom of the flask ; it may be very small ; the second tube, *b*, must be of thin glass, and should be about 4 inches long and half-inch bore. Let its lower end protrude about an inch through the cork. Pack this tube with glass wool. Also pass through the cork a deflagrating spoon, *c*. This should reach as close to the bottom as possible. Fig. 31 shows the apparatus fitted up. Blow through *a* in order to see that air passes readily through *b* in the complete apparatus. Have

also in readiness a gas-bag containing air. Thoroughly dry a piece of phosphorus and place it in the deflagrating spoon. Weigh the whole apparatus as accurately as possible, and note the weight. Lift out the deflagrating spoon, light the phosphorus, and immediately replace it. Connect up the tube *a* with the air-bag. At first the phosphorus burns brightly, but soon the flame grows dim, through exhaustion of the oxygen in the air ; at this stage pass a gentle current of air from the bag through *a* until the phosphorus is entirely burned. The nitrogen escapes through *b*, the phosphorus pentoxide being retained by the glass wool. When the apparatus is cool, again weigh. The experiment being properly performed, the increase of weight is due to the oxidation of the phosphorus.
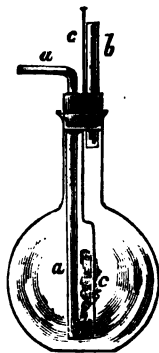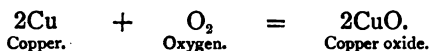
FIG. 45.—Increase of weight caused by burning phosphorus in air.

The oxygen may also be removed by the action of metallic copper. If an iron tube be filled with copper turnings, and made red hot in a furnace, the copper immediately combines with the oxygen of any air which may be passed through, leaving the nitrogen—
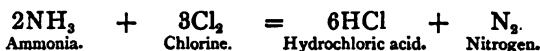
$$2Cu \quad + \quad O_2 \quad = \quad 2CuO.$$
Copper.   Oxygen.   Copper oxide.

Iron likewise removes the oxygen from air, especially if it be caused to oxidize more readily by the addition of some ammonium chloride.

Experiment 133.—Introduce into a gas-jar some iron borings, moistened with a strong solution of ammonium chloride (sal-ammoniac), and closely stop the jar with a glass plate or accurately fitting cork. Let it remain until the filings have rusted, then test the residual gas with a taper. It immediately extinguishes it, giving all the reactions of nitrogen.

There are several other methods of preparing nitrogen which are interesting from a theoretical point of view. For
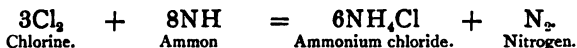
instance, the gas is evolved by passing chlorine into an excess of ammonia. The hydrogen and chlorine unite, and nitrogen is liberated—

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Nitrogen.}}{N_2.}$$

A secondary reaction goes on between the acid formed and the excess of ammonia; thus—

$$\underset{\text{Ammonia.}}{6NH_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Ammonium chloride.}}{6NH_4Cl.}$$

The two equations may be grouped into one; thus—

$$\underset{\text{Chlorine.}}{3Cl_2} + \underset{\text{Ammon}}{8NH} = \underset{\text{Ammonium chloride.}}{6NH_4Cl} + \underset{\text{Nitrogen.}}{N_2.}$$
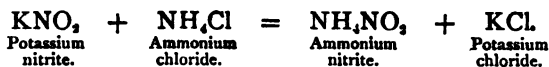
Experiment 134.—Prepare a flask for the evolution of chlorine; arrange a second flask as a wash-bottle with the delivery tube very wide, and place in it 2 or 3 oz. of strongest solution of ammonia; connect to the chlorine flask, and to the delivery tube of the wash-bottle attach a large-diameter piece of tubing leading into the pneumatic trough. Heat the chlorine mixture; as each bubble passes into the ammonia, dense white fumes of ammonium chloride are produced; a wide leading tube is used, because a narrow one might be choked by accumulation of this salt. Considerable heat is evolved, and the action is so intense that flashes of light accompany the combination of the chlorine and hydrogen. Collect one small jar only of the nitrogen which passes over, and apply a lighted taper: the light is extinguished, and the gas does not take fire. Unless strict attention be paid to the laboratory hints at the end of the chapter, this experiment becomes dangerous.

Another interesting method of preparing nitrogen is by the action of heat on the salt known as ammonium nitrite. This contains oxygen and hydrogen in the proportions necessary to form water: they combine and nitrogen is liberated—

$$\underset{\text{Ammonium nitrite.}}{NH_4NO_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2.}$$
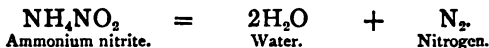
It is usual to prepare the ammonium nitrite at the time of the experiment, that body being somewhat unstable. Ammonium chloride being added to potassium nitrite, the following decomposition takes place :—

$$\underset{\substack{\text{Potassium} \\ \text{nitrite.}}}{\text{KNO}_2} + \underset{\substack{\text{Ammonium} \\ \text{chloride.}}}{\text{NH}_4\text{Cl}} = \underset{\substack{\text{Ammonium} \\ \text{nitrite.}}}{\text{NH}_4\text{NO}_2} + \underset{\substack{\text{Potassium} \\ \text{chloride.}}}{\text{KCl.}}$$

Experiment 135.—Take a 4-oz. flask fitted with a cork, through which passes a single leading tube ; put in about a quarter of an ounce of potassium nitrite and an ounce of saturated solution of ammonium chloride in water ; arrange a jar for the collection of the gas, and apply heat ; the nitrogen comes over readily. The potassium chloride remains unaltered in the flask. Again test the gas by placing in it a lighted taper ; also introduce some litmus paper : notice that the gas is neutral.

149. Properties.—Nitrogen differs remarkably in properties from oxygen, with which it is associated in the atmosphere. The one is specially characterized by its great chemical activity; the other is most inactive. It is a colourless, odourless, neutral, and tasteless gas, which is neither inflammable nor a supporter of combustion. It is not poisonous, but is unable to support life. Animals placed in it speedily die through suffocation. By the action of intense heat it may be caused to combine with oxygen, to form a ruddy-coloured gas, nitrogen peroxide, NO_2, which, by uniting with more oxygen and water, produces nitric acid. Small quantities of nitric acid are thus produced in the atmosphere by lightning discharges. The effect may be imitated on the small scale by passing a series of sparks from an induction coil through moist air contained in a small glass globe. The air assumes a faint red tint, and litmus paper placed in the globe shows that it possesses an acid reaction.

Experiment 136. — Procure a globe properly prepared with platinum wires through the sides ; introduce a piece of

moistened blue litmus paper; cork up the vessel, and pass through it for about ten minutes a current of sparks from the induction coil; notice that the effects described above are produced.

Nitrogen is but slightly soluble in water: 100 volumes at 0° C. dissolve but 1·48 volumes of this gas.

The Atmosphere.—A gaseous mixture. Density, 14·47. Specific gravity, 1·00.

150. Occurrence.—This gaseous body, which envelops the earth, is of vast importance to us who live and breathe in it. Its existence is demonstrated whenever it is set in rapid motion, as we then have winds; and these when sufficiently violent produce well-known and striking physical effects. That air, among the other properties of matter, possesses weight has already been demonstrated by experiment.

151. Composition.—The composition of the atmosphere has been made the subject of many careful experiments, which show it to be a mixture of nitrogen and oxygen approximately in the proportion of four to one. A rough kind of analysis of air has been already made by the student, the oxygen being removed by phosphorus. In addition to these two elements, there are also present varying quantities of aqueous vapour, carbon dioxide, ammonia, nitric acid, and traces of other bodies. Its average composition in England is approximately shown in the following table :—

Oxygen	20·61
Nitrogen . . .	77·95
Carbon dioxide . . .	0·04
Aqueous vapour. . .	1·40
Nitric acid . . .	
Ammonia . . . . }	Traces
Carburetted hydrogen .	
In {Sulphuretted hydrogen . }	
towns{Sulphur dioxide . . . }	,,

The proportion of nitrogen to oxygen in air is remarkably constant, but little variation from the above being found in air collected in the most varied localities; still slight but marked differences are observed in samples collected from different sources. The results of careful analyses of air, freed from carbon dioxide and aqueous vapour, give the following average composition :—

			By measure.	By weight.
Nitrogen	.	.	79·19	76·99
Oxygen .	.	.	20·81	23·01
			100·00	100·00

The composition by volume may be determined by using a eudiometer tube similar to that used in Exp. 61, Fig. 28, for showing the production of water by the union of oxygen and hydrogen. A measured quantity of air is placed in the eudiometer, and hydrogen added in excess of that necessary to combine with the whole of the oxygen present; on the passage of a spark, union of the hydrogen and oxygen is effected, and on the gas regaining its original temperature, the volume is found to be much less. As water is composed of two volumes of hydrogen to one of oxygen, the amount of oxygen present in the gaseous mixture is one-third of the diminution observed. The eudiometer employed for this purpose should be graduated. Supposing that 10 c.c. of air have been introduced and 5 c.c. of hydrogen added; after the explosion the volume will be found to be reduced from 15 to about 9 c.c.; 10 c.c. of air therefore contain approximately $\frac{6}{3} = 2$ c.c. of oxygen, the more accurate figures being those given above.

The composition by weight is ascertained by passing air over red-hot copper, due precautions being taken to avoid error. The copper is placed in a piece of difficultly fusible glass tubing, with which it is weighed; an exhausted receiver is also weighed and attached to one end of this tube; the

R

other is connected with U tubes filled with caustic potash
and sulphuric acid respectively, for the purpose of removing
carbon dioxide and water. The glass tubing is raised to red
heat, the stop-cock of the receiver is opened, and a slow
current of air passes over the copper; its oxygen is removed,
and nitrogen only passes into the empty receiver. The
gain in weight of the copper represents the weight of oxygen,
and that of the receiver the weight of nitrogen.

152. Air a Mixture.—That air is a mixture and not a
compound may be proved in many ways. In the first place,
the oxygen and nitrogen are not present in any simple
multiple of their atomic weights, which is a necessity in all
compounds. Air also differs remarkably from those com-
pounds of the two elements with which chemists are
acquainted. If a mixture be made of nitrogen and oxygen
in the proportion in which they exist in air, no alteration
of volume takes place, neither is there any increase of
temperature; the mixture exhibits all the properties of air.

Experiment 137.—Mix in a gas-jar in the pneumatic trough
four volumes of nitrogen with one of oxygen; introduce a
lighted taper : it continues to burn exactly the same as in air.

The most conclusive evidence of their being mixed, and
not combined, is that they may be separated by the action
of water as a solvent. Oxygen is more soluble than nitro-
gen, and if water which has been previously freed from
gases by boiling be shaken up with air, and then again
boiled, the expelled gas is found on analysis to be much
richer in oxygen than was the air, the oxygen amounting to
about 34 per cent. of the dissolved gases.

It will be interesting here to note the difference between
air on the one hand and water on the other. In air the
two most important constituents are not present in the same
absolutely unvarying proportion. On oxygen and nitrogen
being mixed in the same proportions as they exist in air,
no alteration in volume occurs, and the mixture exhibits

properties which are a mean of those of the two ingredients. Further, they may be separated by the action of water as a solvent.

With water the hydrogen and oxygen are always present in absolutely unvarying proportions. When these gases are mixed and a light applied, a violent explosion occurs; the water produced condenses to a liquid possessing properties altogether different from those of its constituents. The explanation is that air is a mixture, and water a chemical compound.

153. Argon.—Among the constituents of air a new elementary gas has recently been discovered, to which the name of "Argon" has been given. The gas closely resembles nitrogen in its properties, which at present are under investigation.

154. Functions of Atmospheric Carbon Dioxide.—It has already, in Chapter XIII., been pointed out that carbon dioxide is present in air, and that the breathing of animals and the burning of carbonaceous bodies are continually supplying this gas; although this operation is proceeding without intermission, the quantity of carbon dioxide present in the atmosphere remains remarkably constant. Its amount varies between 3 and 6 parts in 10,000 according to the locality where, and time when, the gas is collected. This quantity, though small, is of vast importance to the vegetable kingdom, as it is the source from which all organic carbon is derived in nature. Animals can only assimilate carbon from previously existing organic compounds. Vegetables decompose carbon dioxide, using the carbon in the formation of their tissues, and liberating the oxygen in the free state.

Experiment 138.—Take a beaker some ten or twelve inches high, and arrange in it some sprigs of fresh mint or some other quickly growing plant immediately after being cut, or preferably pulled up with the roots attached. In this latter case, first

wash the roots in a gentle stream of water. Fill the beaker with water through which washed carbon dioxide gas has been passed to saturation. Fix an inverted funnel over the sprigs of mint, so that the top of the funnel is entirely submerged. Fill a test-tube with water, and place it over the funnel, so as to retain any gas that may be given off. Place the whole apparatus in direct sunlight. The growing mint decomposes the carbon dioxide dissolved in the water; the oxygen which escapes is caught as it rises by the funnel, and collects in the test-tube. After some hours, test the evolved gas with a glowing splinter; it gives the reaction of oxygen.

The effects, therefore, of animal and vegetable life on the atmosphere are opposite in character: the one removes oxygen and returns carbon dioxide, the other decomposes this compound, and again yields oxygen to the air (this return action is, however, partially balanced by the ordinary progress of decay); these two processes going on simultaneously keep the proportion of carbon dioxide in air within constant limits. The decomposition of certain rock-forming minerals, as felspar, by the action of the carbon dioxide of the atmosphere, which combines with the bases that they contain, is another important drain on the amount of that gas present in air.

155. Other Constituents.—The amount of aqueous vapour which the atmosphere contains varies considerably; but it is always present in more or less quantity. Its presence may be demonstrated by bringing a vessel of ice-cold water into a room: the aqueous vapour condenses on the outside as a film of moisture.

Ammonia is only found in air in minute traces. These, however, are important, as from them plants obtain a great proportion of their nitrogen.

Summary.

Nitrogen exists in the free state in the atmosphere, and is also found in nitrates and different organic bodies. It is prepared either by the removal of oxygen from the air by the

action of phosphorus or copper, or by the decomposition of bodies containing nitrogen, as ammonium nitrate and ammonia. Nitrogen is a colourless, odourless, and tasteless gas ; is neither inflammable nor a supporter of combustion ; is neutral to litmus paper ; by great heat may be made to combine with oxygen, forming acid compounds.

The atmosphere is a mixture of nitrogen and oxygen, with small quantities of other compounds present. Its composition is determined by explosion with hydrogen and other methods. Air is a mixture, proved by different solubility of the two gases in water.

Carbon dioxide is produced by the breathing of animals and burning of substances containing carbon. The same gas is removed by the action of vegetable life, and oxygen restored to the air.

The ammonia present in air supplies nitrogen to plants.

OBJECT DEMONSTRATION.

Observe and note appearance and physical characters of iron borings and ammonium chloride (sal-ammoniac). Examine, if possible, pieces of weathered granite and felspar.

LABORATORY DIRECTIONS.
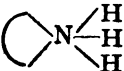
In preparing nitrogen by the action of chlorine or ammonia, strict attention must be paid to the directions *always to have excess of ammonia :* see accordingly that the solution used is the strongest, of specific gravity 0·88, and not the dilute solution employed in the laboratory for analytical purposes. Prepare but one jar of the gas by this method. These precautions are necessary, because with excess of chlorine a most violently explosive compound of nitrogen and chlorine is formed. The wide leading tube is also an essential. The glass globe with platinum wires passed through, used in Exp. 136, should be obtained from the general apparatus of the laboratory ; they can be bought of any apparatus dealer ; the form sold is, however, somewhat fragile, and not well suited for the rough usage of a laboratory. One may be easily prepared by taking a 3 or 4-oz. wide-mouthed bottle, fitting it with a cork, through which is passed two pieces of quill glass tubing in which platinum wires are fused. The ends of the wires should be about an

eighth of an inch apart, and reach to the middle of the bottle: the glass tubes are to be filled with mercury; the connection with the coil is made by dipping the *clean* ends of the leading wires underneath its surface. The cork should be soaked in melted paraffin. The apparatus as thus constructed bears some resemblance to that described for the electrolysis of water in Exp. 58 (Fig. 23). Remember, when the cork is taken out of the bottle, to so place it that the mercury does not run out of the tubes.

CHAPTER XVI,

AMMONIA.

Formula, NH_3. Molecular weight, 17·01. Density, 8·5,
Specific gravity, 0·59.

Graphic formula, $\bigcirc\!\!>\!\!N\!\!<^{\displaystyle H}_{\displaystyle H}\!\!-H$

156. Occurrence.—This, the only compound of nitro-
gen and hydrogen known in the free state, exists in small
quantities in the atmosphere, and also in rain-water. It is
probably a resultant product of the oxidation of different
organic substances in the presence of moist air. The
oxygen of the water acts as the oxidizing agent, and the
nascent hydrogen combines with nitrogen to form small
quantities of ammonia. It is produced in considerable
quantity in the decomposition of animal and vegetable
bodies which contain nitrogen. The urine and excreta of
animals contain refuse nitrogenous matter. This after a
time becomes changed into ammonia, and thus causes these
substances to be such valuable manures, as plants are in-
capable of assimilating nitrogen while free, but are able to
do so when that element is presented to them as ammonia.

The name ammonia is derived from that of Jupiter
Ammon, because near a temple dedicated to him the Arabs
extracted one of its compounds from camel's dung. If
quills, horn, hair, etc., be heated in a closed vessel, various
gases are evolved, among which ammonia is always present.

Experiment 139.—Heat in a test-tube some hair or quill cuttings ; place a piece of red litmus paper in the condensed moisture in the upper part of the tube : it is turned blue.

Coal contains about 2 per cent. of nitrogen, and in like manner evolves ammonia when heated. As this substance is subjected to destructive distillation on the large scale in the manufacture of coal gas, it affords a cheap and plentiful source of ammonia. The ammonia passes over with the gas, and is dissolved by the condensed moisture. This constitutes the gas or ammoniacal liquor of the works. From this, ammoniacal salts are prepared by the addition of acids.

157. Preparation.—Nitrogen and hydrogen do not unite readily, but may be caused to do so by passing a series of electric sparks from an induction coil through a mixture of the two gases. It is not possible in this way to cause the union of the whole of the nitrogen and hydrogen present unless the ammonia is removed as rapidly as formed, because as soon as a considerable proportion of ammonia is present the heat of the sparks once more causes its decomposition into free nitrogen and hydrogen. The ammonia may be removed in this experiment by causing the reaction to take place over a solution of hydrochloric acid, which combines with the ammonia to form ammonium chloride.

Ammonia may be prepared from any of the ammoniacal salts by heating with a stronger base, as lime or soda. Of these lime is preferred because of its cheapness. If ammonium chloride and lime be heated together, the following reaction takes place :—

$$2NH_4Cl \quad + \quad CaO \quad = \quad CaCl_2 \quad + \quad H_2O \quad + \quad 2NH_3.$$
Ammonium   Quicklime.   Calcium   Water.   Ammonia.
chloride.   chloride.
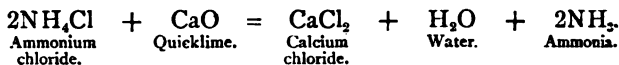
Experiment 140.—Fit to an 8-oz. flask a cork with single delivery tube, to which is attached, by means of a moderately long piece of indiarubber tubing, a glass tube about a foot in length. The flask, tubing, and all other apparatus must be

perfectly dry. Dry separately some powdered lime and ammonium chloride (sal-ammoniac); the lime may be dried by simply heating in a sand-bath; to dry the ammonium chloride, place it in an evaporating basin and heat gently either on the sand-bath or on a piece of wire gauze over the Bunsen flame turned down very small; the heat must not be sufficient to cause any fumes to be evolved. This may be set to dry before preparing the flask. They must be allowed to cool; then take about half an ounce of the ammonium chloride and an ounce of the lime. Mix intimately in the mortar the chloride and
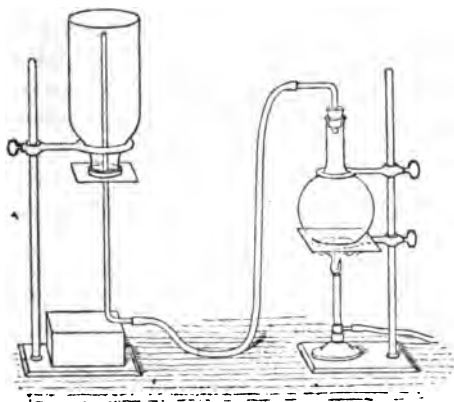
FIG. 46.—Preparation of ammonia.

about two-thirds of the lime; notice that ammonia is given off by its smell; pour the mixture into the flask, and then add the remaining lime in a layer over the top. Fix the flask in the retort stand, with a piece of gauze underneath; arrange the leading tube upright, so that gas may be collected by upward displacement; invert a dry gas-bottle over the tube, the end of which must reach right up to the top. Fig. 46 shows the whole arrangement. The gas-bottle is most conveniently held on the ring of a retort stand. Apply a gentle heat to the flask; the gas is evolved readily. To test when the jar is full, hold a piece of reddened litmus paper outside the bottle just above the mouth; it will be turned blue. Draw the tube out of the bottle, lift it from the ring, and quickly

place on the cover.   Three jars of gas should be in this way collected.

Experiment 141.—Then place the end of the delivery tube in a little distilled water in a beaker ; notice that the whole of the gas is absorbed.   In two or three minutes remove the tube and withdraw the Bunsen from the flask ; the liquid smells of the gas.   To some litmus solution in a test-tube add a drop of sulphuric or hydrochloric acid so as to just redden it ; to this add the ammonia solution ; the blue colour is restored.

158. Properties.—Ammonia is a colourless gas with a most pungent and characteristic odour, which is pleasant when the gas is mixed with air ; but in the undiluted state the gas acts as a powerful irritant, bringing tears to the eyes, and if accidentally inhaled, even in small quantities, destroys the surface of the mucous membrane of the mouth, and may produce even fatal effects by its action on the lungs. The solution in water has a burning and disagreeable taste. The gas may be condensed to a liquid by a temperature of $-50°$ C., or a pressure of about 7 atmospheres at $15°$ C. Like other liquefied gases, liquid ammonia is very volatile, producing great cold in evaporating.   This property causes it to be largely used in the manufacture of artificial ice. The gas is remarkably soluble in water, which dissolves at $0°$ C. 1050 times its volume of the gas ; at $15°$ C. 727 volumes.   The concentrated solution readily evolves gas on being heated, and may frequently be used with advantage as a source of the gas.   At ordinary temperatures the solution gives off gas, hence its pungent odour.   A solution of hydrochloric acid in water has a higher specific gravity than water, while that of ammonia is lower.   The concentrated solution at $15°$ C. has a specific gravity of 0·880.

Experiment 142.—Place the mouth of one of the jars of gas under water, and remove the glass plate ; the water rushes up with violence and fills the jar.

It has been before mentioned that charcoal possesses the property of absorbing gases : ammonia is a striking

example. Freshly burned charcoal absorbs about 90 volumes of this gas.

Experiment 143.—Take a dry 6-inch test-tube, fill it with mercury in a mercury trough, and fix in a retort stand with the mouth under the surface. In a clean 4-oz. flask place about an ounce of concentrated ammonia solution, fit to it a cork with single delivery tube, leading into the mercury trough, fix the flask in the retort stand, and apply a gentle heat ; gas comes over almost immediately ; wait until the air is all expelled, and then fill the test-tube with gas. Select a piece of charcoal of a size that will easily go into the tube ; heat it in the Bunsen, and then by means of the tongs introduce it through the mercury into the gas ; it rapidly absorbs it, and the mercury rises to the top of the tube.

Ammonia is a non-supporter of combustion, and non-inflammable at ordinary temperatures ; but when heated it takes fire and burns with a greenish flame ; water is produced and nitrogen set free.
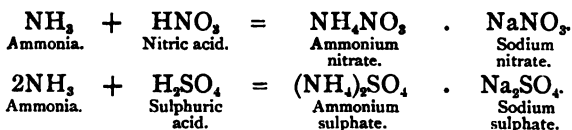
$$4NH_3 \quad + \quad 3O_2 \quad = \quad 2N_2 \quad + \quad 6H_2O.$$

Ammonia.   Oxygen.   Nitrogen.   Water.
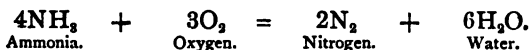
Experiment 144.—Place a lighted taper in a jar of the gas ; the taper goes out, but just before doing so the flame slightly enlarges and becomes of a green colour.

Experiment 145.—Place in the furnace an iron tube fitted with corks and pieces of quill tube at each end ; when the tube is red hot, connect to it the 4-oz. flask containing ammonia solution ; apply heat and light the gas as it emerges from the iron tube ; it burns with a green flame.

It has already been seen by experiment that ammonia restores the blue colour to litmus. It neutralizes the strongest acids, and forms a well-marked and most important series of salts. The composition of some of these is thus shown :—

$$NH_3 \quad + \quad HCl \quad = \quad NH_4Cl \quad . \quad NaCl.$$

Ammonia.   Hydrochloric   Ammonium   Sodium
         acid.   chloride,   chloride.

$$NH_3 \quad + \quad HNO_3 \quad = \quad NH_4NO_3 \quad . \quad NaNO_3.$$

Ammonia.   Nitric acid.   Ammonium   Sodium
                                       nitrate.   nitrate.

$$2NH_3 \quad + \quad H_2SO_4 \quad = \quad (NH_4)_2SO_4 \quad . \quad Na_2SO_4.$$

Ammonia.   Sulphuric   Ammonium   Sodium
                  acid.   sulphate.   sulphate.
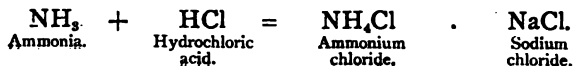
The salts of sodium are also written in a separate column for the sake of comparison. It will be seen that the group NH_4 and sodium occupy corresponding places. Further, this group may be expelled from one chemical compound and caused to enter another without decomposition.

159. Compound Radicals.—This is only one instance of a group of elements entering into the composition of a body, and performing functions very similar to those of an atom of an element. Such groups are not only found to form numbers of very definite compounds, but may be even transferred from one compound to another without undergoing decomposition. **Groups of atoms of different elements which possess a distinct individuality throughout a series of compounds, and behave therein as though they were elementary bodies, are termed "compound radicals."**

160. Ammonium and its Salts.—The group NH_4 is one of the best and most striking examples of a compound radical; because it thus behaves in so many compounds as though it were an element, it has received a name *ammonium*, for which the symbol Am is sometimes used. Ammonium chloride is written either NH_4Cl or AmCl. Ammonium, however, cannot be isolated, but immediately splits up into ammonia and free hydrogen. The solution of ammonia in water is sometimes conveniently represented as a hydrate of ammonium; thus—

$$NH_3 \quad + \quad H_2O \quad = \quad NH_4HO.$$

Ammonia.   Water.   Ammonium hydrate
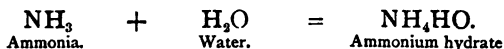
This, again, is analogous in composition to sodium hydrate, NaHO.

Ammonium hydrate produces in many cases the same

chemical reaction as does either sodium or potassium hydrate. Thus all these bodies produce the same precipitate of ferric hydrate, $Fe_2(HO)_6$, from a solution of ferric chloride, Fe_2Cl_6. The student is referred to the analytic section of this work for an account of these reactions.

The principle of the preparation of ammonia is simply, therefore, to displace it from a salt by the action of a stronger and non-volatile base, as lime. The action is similar to that in which a volatile acid, as hydrochloric, is displaced by a less volatile and more powerful acid, as sulphuric.

The salts of ammonium are formed, as shown by equations, by the direct union of the acid with gaseous ammonia,

Experiment 146.—Fill a bottle with hydrochloric acid gas, place it over the remaining bottle of ammonia, remove the plates, bringing the mouths of the bottles together ; a dense white cloud of ammonium chloride is formed ; the bottles get sensibly warm to the hand.

Salts of ammonia with volatile acids may in some cases be sublimed without the production of any permanent chemical change, as with ammonium chloride. Others are decomposed, as ammonium nitrate ; those with non-volatile acids, as ammonium phosphate, are decomposed ; the acid remains, and free ammonia is evolved.

Experiment 147.—Heat a little ammonium chloride in a test-tube ; the salt, if pure, entirely sublimes, and recondenses in the upper part of the tube. In a second tube heat some ammonium phosphate : free ammonia is evolved, and phosphoric acid remains.

161. Composition.—The composition of ammonia by volume may be ascertained by passing a series of electric sparks through the gas in a eudiometer. Any residual ammonia which has escaped decomposition, must be absorbed by caustic potash. The volume of the remaining gas is double that of the ammonia from which it has been formed, two molecules of ammonia producing one molecule

of nitrogen and three of hydrogen. The quantity of hydrogen is determined by adding excess of oxygen and exploding. It amounts to two-thirds of the diminution. The excess of oxygen is then removed by adding pyrogallic acid and caustic potash, by which it is absorbed; the residual gas is nitrogen.

The composition by weight may be ascertained by passing a measured quantity of dry ammonia over red-hot copper oxide; water is formed, and may be collected by calcium chloride. Nitrogen passes over in the free state. The hydrogen is calculated from the water, and the difference of weight between that and the ammonia represents the nitrogen.

Experiment 148.—Pass a current of dry ammonia over copper oxide, heated to redness in a combustion tube. Note that water is formed, and that the oxide is reduced to the metallic state.

Pass a mixture of air and ammonia over the red-hot copper remaining in the tube, and collect the gas which escapes. On testing, it is found to be nitrogen.

In this latter part of the experiment the oxygen of the air and the hydrogen of the ammonia unite to form water; the atmospheric nitrogen and that contained in the ammonia both escape together.

Summary.

Ammonia exists in traces in the atmosphere; is formed by the decomposition of nitrogenous organic matter; is manufactured from the watery distillate of the gaswork, by neutralizing with acid, and subsequently treating the salt produced with lime and heating.

Ammonia is a colourless gas, with characteristic odour; may be liquefied by pressure or cold; is very soluble in water, and is also absorbed in large quantities by charcoal. The gas is a non-supporter of combustion, and is non-inflammable at ordinary temperatures; but when heated burns with a greenish flame. It is alkaline to litmus paper, and forms with acids a

series of salts in which NH_4 occupies the place of a monad metal. This group has received the name ammonium and symbol Am ; does not exist in the free state, but breaks up into ammonia and hydrogen. Ammonium salts are volatile if the acid be so ; those with a fixed acid are decomposed ; the acid remains, and ammonia is evolved.

The decomposition is determined by decomposing the gas by electricity and estimating the hydrogen and nitrogen.

OBJECT DEMONSTRATION.

Note appearance and character of a sample of guano, and of ammoniacal gas-liquor. Observe ammoniacal odour of each. Examine a series of ammoniacal and corresponding potassium or sodium salts.

LABORATORY HINTS.

In preparing ammonia from the chloride and lime, unless both are dried, there is a danger of breaking the flask by water condensing in the upper parts and trickling down on the hot glass. It is a good plan to place two pieces of gauze under the flask, and to use a rose burner if you have one ; otherwise keep the flame small. When collecting a gas by displacement, it is advisable to have a piece of cardboard closing the mouth of the jar, with a slit through it for the leading tube : this is kept on the mouth until the glass plate is exchanged for it.

When the end of the leading tube is placed in water, watch carefully to see that the gas is not absorbed so rapidly as to cause the water to rise in the tube ; should it have a tendency to do so, increase the heat, and, if necessary, take away the beaker of water, and draw the cork from the flask. In any case remove the beaker *before* the flame.

There is a difficulty in filling jars in the mercury trough through not being able to see the end of the leading tube ; this should be bent up at an acute angle, and may then be hooked into the mouth of the tube. A tube of stouter glass than that of the test-tube is much better, and may be made by drawing out a piece of glass tubing.

162. Nitrogen Oxides.—There are five compounds of nitrogen and oxygen known, two of which, by union with water, form acids : their names and composition are—
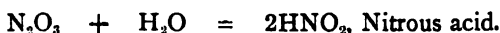
Nitrogen monoxide, or nitrous oxide, N_2O.
Nitrogen dioxide, or nitric oxide, NO (or N_2O_2).
Nitrogen trioxide, or nitrous anhydride, N_2O_3.
Nitrogen tetroxide, or nitric peroxide, NO_2 (or N_2O_4).
Nitrogen pentoxide, or nitric anhydride, N_2O_5.

By the action of water we have—

$$N_2O_3 \quad + \quad H_2O \quad = \quad 2HNO_2, \text{ Nitrous acid.}$$
$$N_2O_5 \quad + \quad H_2O \quad = \quad 2HNO_3, \text{ Nitric acid.}$$

This series of compounds is interesting because it affords such a striking illustration of the law of multiple proportions ; 28 parts by weight of nitrogen combine respectively with 16, 32, 48, 64, and 80 parts of oxygen.

Nitric acid is by far the most important of these bodies, and as the whole of the others are prepared from it, nitric acid is conveniently studied first.

Nitric Acid.—**Formula, HNO_3. Molecular weight, 62·89. Specific gravity of liquid, 1·52. Melting-point, about −55° C. Boiling-point, 84·5°.**

163. Occurrence.—Nitric acid is produced in small quantities in the atmosphere, from which it is separated by

rain, which therefore usually exhibits traces of this acid when subjected to analysis. The salts of nitric acid with soda and potash (sodium and potassium nitrates) are its most common sources. Layers of potassium nitrate are found incrusting the soil in India, and of sodium nitrate in parts of Chili and Peru; the latter of these is the more plentiful. These nitrates are produced by the oxidation of nitrogenous organic matter in the presence of the bases potash or soda. Potassium nitrate is also known as saltpetre or nitre; sodium nitrate is frequently called Chili saltpetre or cubic nitre, from the shape of its crystals.

164. Preparation.—Nitric acid is always prepared by the action of sulphuric acid on a nitrate, usually either that
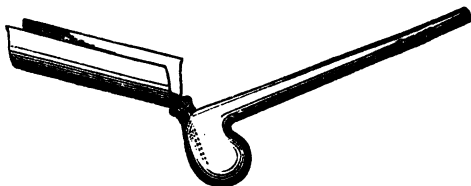
FIG. 47.—Method of filling retort.

of sodium or potassium. The two are mixed in a retort, and on the application of heat nitric acid, being more volatile, distils over, leaving acid sodium sulphate—

$$NaNO_3 \; + \; H_2SO_4 \; = \; HNO_3 \; + \; NaHSO_4.$$

Sodium nitrate.   Sulphuric acid.   Nitric acid.   Acid sodium sulphate.
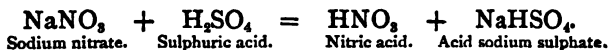
Experiment 149.—Take a 4 or 6-oz. stoppered retort, get it thoroughly clean, and pour in about an ounce of sodium nitrate through the tubulure (*i.e.* hole for the stopper): this is most easily effected by taking a piece of paper and doubling it up as shown in Fig. 47; the nitrate is placed on this, and carefully transferred to the retort, which should be held as in the figure; on no account must any of the nitrate get into the

Next clean and drain a small flask or 6-inch test-tube, and

S

introduce into it the beak of the retort as represented in Fig. 48. Arrange the apparatus in the retort stand with the test-tube or flask well under water in the pneumatic trough; the further under the better, so that the water does not run into the tube.
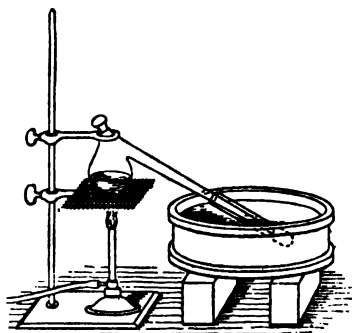

FIG. 48.—Preparation of nitric acid.

The retort must be held securely by a ring passing over the neck. It may be necessary to raise the trough some little distance above the table; adjustments of this kind are best performed by pieces of blocking; the trough should be got to its right place *first*, and then filled with water. Next pour in an ounce of concentrated sulphuric acid, replace the stopper, and apply heat carefully with the Bunsen. The nitrate melts, brownish red fumes are seen in the retort, and a pale yellow liquid distils over into the tube or flask. Collect sufficient to about one-quarter fill a 6-inch test-tube, then remove the light and disconnect the apparatus; pour the sulphate out of the retort into an evaporating basin while still liquid; it solidifies, being nearly pure acid sodium sulphate. Reserve the nitric acid for further experiments.

On the application of a more intense heat, the acid sulphate of sodium is capable of acting on another quantity of the nitrate, with the formation of the normal sulphate—

$$NaHSO_4 \quad + \quad NaNO_3 \quad = \quad Na_2SO_4 \quad + \quad HNO_3.$$

Acid sodium sulphate.   Sodium nitrate.   Sodium sulphate.   Nitric acid.

The temperature necessary for this second reaction, however, partly decomposes the nitric acid produced.

165. Properties.—Nitric acid, when pure, is a colourless fuming liquid, but usually is of a faint yellow tinge through the presence of some of the lower oxides of nitrogen, produced by its partial decomposition. It is an extremely
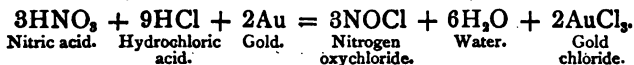
powerful oxidizing agent, and rapidly destroys animal tissues ; it stains the skin, horn, etc., a bright yellow colour. It attacks most of the metals, including copper, mercury, and silver, with great vigour; gold and platinum are unaffected by it, or any single acid (except that gold is oxidized by the rare compound, selenic acid).

Experiment 150.—Fill an iron ladle with small fragments of charcoal, and heat to redness over a powerful Bunsen flame. Fasten a test-tube to the end of a rod, and partly fill with concentrated nitric acid. Pour a little of the acid on to the red-hot charcoal. Vigorous combustion ensues, due to the rapid oxidation of the charcoal by the acid.

Vigorous combustion of this kind is termed *deflagration*.

166. Action of Acids on Gold.—*Experiment* 151.—
Take a small piece of gold leaf and place it in a test-tube, add some nitric acid and heat gently ; the gold is undissolved. Treat another piece similarly with strong hydrochloric acid ; this also is without action. Now mix the two together : the gold dissolves rapidly.

This mixture of acids is generally termed *aqua regia* (royal water), from its power of thus dissolving " the king of metals;" its activity depends on the production of nascent chlorine, which combines with gold forming auric chloride ; the reaction may be represented by the following equation, but varies with the different proportions of hydrochloric and nitric acids which may be used :—

$$3HNO_3 + 9HCl + 2Au = 3NOCl + 6H_2O + 2AuCl_3.$$

| Nitric acid. | Hydrochloric acid. | Gold. | Nitrogen oxychloride. | Water. | Gold chloride. |

167. Action of Nitric Acid ; and Nitrates.—The
action of nitric acid on the metals generally is more complex than that of hydrochloric or sulphuric acids; the nascent hydrogen, displaced by the metal, attacks the remaining nitric acid and forms water, liberating one or more of the lower oxides of nitrogen; the particular one

evolved, and the proportions of each present in a mixture, depend on the metal used, the degree of concentration of the acid, and other causes.

Experiment 152.—To some of the nitric acid distilled in a previous experiment add one or two pieces of copper clippings ; notice that a violent action goes on, ruddy fumes are evolved, and a green solution of copper nitrate formed.

Nitric acid is a monobasic acid, its salts being known as nitrates ; they may be prepared either by acting on the metal, as with copper, or by adding the acid to an oxide or a carbonate.

Experiment 153.—Take about half an ounce of strong nitric acid, place it in a beaker, and add solid ammonium carbonate in small quantities until it no longer causes effervescence ; the liquid now has an alkaline reaction to litmus paper. Add nitric acid drop by drop until the solution is neutral ; place this away for a week in an evaporating basin ; at the end of that time long needles of ammonium nitrate will have crystallized out. The salt must be reserved for a future experiment.

The nitrates, like the acid from which they are derived, are powerful oxidizing agents ; potassium nitrate is used as a source of oxygen in gunpowder, which is a mixture of that compound with sulphur and charcoal.

If charcoal be dropped into melting potassium nitrate, it burns with great brilliancy.

Experiment 154.—Melt some potassium nitrate in a test-tube, drop in a fragment of charcoal ; it burns with evolution of carbon dioxide. The mouth of the tube should be held away from any person, as sometimes the red-hot piece of charcoal jumps out of the tube.

Nitric acid and all the nitrates are decomposed by heat, oxides of the metals remain, and oxygen and nitrogen oxides are driven off.

Experiment 155.—Procure a clay tobacco pipe with very long stem (churchwarden) ; pass the stem through a small gas

tube-furnace, arranged obliquely so that the bowl of the pipe is upwards, and the mouthpiece just beneath the surface of the water of a pneumatic trough. Arrange a test-tube for the collection of gas evolved from the pipe. Pour concentrated nitric acid in the bowl drop by drop ; in passing through the red-hot stem it is decomposed into water, nitrogen peroxide, and free oxygen. The peroxide is dissolved by the water, and oxygen collects in the tube. Test the gas by means of a glowing splinter.

The reaction in the above experiment is represented by the following equation :—

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$
Nitric acid. Water. Nitrogen peroxide. Oxygen.
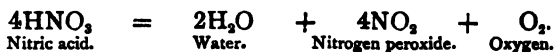
Experiment 156.—Arrange a test-tube with cork and delivery tube, and one-third fill with potassium nitrate. Apply heat, and collect the gas which is evolved. Continue the application of heat until the free evolution of gas ceases. Test the gas by means of a glowing splinter. Reserve the substance remaining in the test-tube for a future experiment.

Potassium nitrate, when heated, undergoes the following change :—

$$2KNO_3 = 2KNO_2 + O_2.$$
Potassium nitrate. Potassium nitrite. Oxygen.

168. Nitric anhydride is an unstable body, and is rarely prepared; it readily unites with water and forms nitric acid—

$$N_2O_5 + H_2O = 2HNO_3.$$
Nitric anhydride. Water. Nitric acid.

Nitrogen Monoxide.—Formula, N_2O. **Molecular weight, 43·98. Density, 21·99. Specific gravity, 1·527.**

169. Preparation.—This gas may be prepared by the action of zinc on dilute nitric acid, the two being gently heated ; the reaction is a somewhat complex one, and may be represented by the following equation :—

$$10HNO_3 + 4Zn = N_2O + 4Zn(NO_3)_2 + 5H_2O.$$
Nitric acid. Zinc. Nitrogen monoxide. Zinc nitrate. Water.

The gas is frequently impure, portions of the nitric acid being reduced to free nitrogen.

Nitrogen monoxide is much more easily obtained by the action of heat on ammonium nitrate, which is decomposed in a manner similar to that in which ammonium nitrite, NH_4NO_2, is separated into water and nitrogen ; the nitrate, however, contains another atom of oxygen (its formula being NH_4NO_3), which is evolved in combination with the nitrogen—

$$NH_4NO_3 \quad = \quad 2H_2O \quad + \quad N_2O.$$
Ammonium nitrate. Water. Nitrogen monoxide.

This equation should be compared with that representing the decomposition of ammonium nitrate.

Experiment 157.—Take an 8-oz. flask, fitted with cork and single leading tube ; transfer to it the ammonium nitrate prepared according to directions previously given ; pour in the saturated solution of the salt as well as the crystals which have formed ; get ready a trough of *warm* water for the collection of the gas, fix the flask into the retort stand, place the end of the leading tube in the trough, and apply heat. At first air escapes and bubbles through the water in the trough ; this is soon displaced by the steam resulting from the evaporation of the water present with the nitrate ; as this enters the colder water it is condensed, and no bubbles arise. In a short time the whole of the water is driven off; at this point the liquid becomes pasty and froths up. Watch carefully, and if necessary remove the light; it soon again subsides, and then evolves gas quietly. Use a flame not too large, but just at such a height as to produce a steady and slow current of gas. Collect three jars for experiment. Take the leading tube out of the trough, remove the Bunsen, and allow the flask to cool : any ammonium nitrate which then remains readily dissolves if some water is placed in the flask.

170. Properties.—Nitrogen monoxide is colourless, has a faint sweetish smell and taste ; it is soluble in cold water ; 1 volume at 15° C. dissolves 0·77 volume of the gas. It may be condensed to a liquid by a pressure of

thirty atmospheres at 0° C., or at ordinary pressures at a temperature of −99° C. Nitrogen monoxide supports combustion almost as vigorously as oxygen ; oxides are formed, and nitrogen liberated. Carbon thus forms carbon dioxide—

$$C \quad + \quad 2N_2O \quad = \quad CO_2 \quad + \quad 2N_2.$$
Carbon.   Nitrogen monoxide.   Carbon dioxide.   Nitrogen.
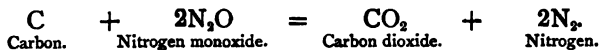
Experiment 158.—Introduce into a jar of the gas a glowing splinter of wood ; it bursts into flame as though placed in oxygen.

The two gases, oxygen and nitrogen monoxide, may, however, be readily distinguished from each other by the much greater solubility of the latter gas, and also by the difference in their behaviour with nitric oxide, to which reference will again be made. In actual analysis the presence of a residue of nitrogen after combustion would also distinguish nitrous oxide from oxygen.

The decomposition of nitrogen monoxide into free oxygen and nitrogen is necessary before bodies can burn in this gas ; if the heat of the combustion is not sufficient to effect this, burning does not go on. Thus feebly burning sulphur is extinguished by the gas, but when burning brightly it continues to do so almost as vividly as in oxygen.

Experiment 159.—Place a piece of sulphur in a deflagrating spoon, let it just take fire in the Bunsen, and plunge it into a jar of the gas ; the light is extinguished. Replace the cover of the gas-jar, and heat the sulphur in the flame until almost boiling, now again place in the gas ; it continues to burn.

$$S_2 \quad + \quad 4N_2O \quad = \quad 2SO_2 \quad + \quad 4N_2.$$
Sulphur.   Nitrogen monoxide.   Sulphur dioxide.   Nitrogen.
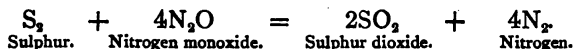
Nitrogen monoxide behaves as an anæsthetic when breathed (*i.e.* a substance which causes insensibility to pain). Some four or five gallons of the gas are sufficient in most cases to produce total insensibility ; before this stage it in

many persons causes a kind of intoxication, often accompanied by violent fits of laughter; because of this it has received the popular name of "laughing gas."
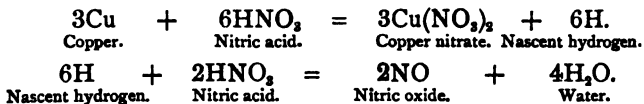
171. Composition.—The molecule of nitrogen monoxide yields a molecule of nitrogen; therefore any quantity of the gas when decomposed produces its own volume of nitrogen; the composition may be determined by exploding the gas in the eudiometer with excess of hydrogen—

$$N_2O \quad + \quad H_2 \quad = \quad N_2 \quad + \quad H_2O.$$

Nitrogen monoxide. Hydrogen. Nitrogen. Water.

A corresponding volume of nitrogen remains to that of the monoxide taken; the diminution in volume consists of hydrogen which has combined with the oxygen; it is necessary, however, to measure the excess of hydrogen which remains in order to deduce the composition of nitrogen monoxide from this experiment.

Nitrogen Dioxide, or Nitric Oxide.—Formula, NO (or N_2O_2). Molecular weight, 29·97. Density, 14·98. Specific gravity, 13·09.

172. Preparation.—This gas is readily obtained by the action of copper on moderately concentrated nitric acid; the reaction occurs without the application of heat: hydrogen is probably first liberated, and then reduces some of the remaining acid—

$$3Cu \quad + \quad 6HNO_3 \quad = \quad 3Cu(NO_3)_2 \quad + \quad 6H.$$

Copper. Nitric acid. Copper nitrate. Nascent hydrogen.

$$6H \quad + \quad 2HNO_3 \quad = \quad 2NO \quad + \quad 4H_2O.$$

Nascent hydrogen. Nitric acid. Nitric oxide. Water.

Or the two reactions may be stated in the one equation.

$$3Cu \quad + \quad 8HNO_3 \quad = \quad 3Cu(NO_3)_2 \quad + \quad 2NO \quad + \quad 4H_2O.$$

Copper. Nitric acid. Copper nitrate. Nitric oxide. Water.

Experiment 160.—Take the flask and delivery tube used for the preparation of hydrogen, No. 2, Fig. 18, and place in it

about half an ounce of copper clippings. Dip the cork of the
apparatus in melted paraffin, and attach a glass leading tube
to the delivery tube, so that the ends are in contact, by a small
piece of indiarubber tubing about 2 inches long. Nitric acid
rapidly corrodes both indiarubber and cork, so that we avoid,
as far as possible, exposing either to its influence ; the paraffin
protects the cork, and the leading tube is practically of glass
throughout. Arrange for the collection of gas over cold water in
the pneumatic trough. Pour on to the copper some of a mixture
of strong nitric acid and water in equal volumes (about 2 oz.) ;
bubbles of gas are evolved, and the whole flask rapidly fills
with red fumes. These soon become lighter in colour, and
as each bubble of gas rises through the water in the trough into
the air, it assumes a dark red tint. The air is now expelled from
the flask, and the gas-jars may be filled ; four will be required
for experiment. If the action slackens before the whole of them
have been filled, add some more of the nitric acid. As the action
goes on with great rapidity, as many jars as possible should be
filled with water and placed inverted in the trough before
the acid is poured on the copper. Remember the order in
which the jars are filled. This experiment should, if possible,
be performed in a stink closet.

This gas may also be prepared by the action of sulphuric
acid on potassium nitrite, when the following reactions
occur :—

$$2KNO_2 \quad + \quad H_2SO_4 \quad = \quad K_2SO_4 \quad + \quad 2HNO_2.$$
Potassium nitrite.   Sulphuric acid.   Potassium sulphate.   Nitrous acid.
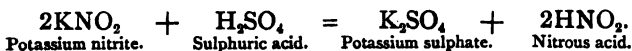
The nitrous acid, if slightly heated, immediately under-
goes decomposition, with the formation of nitric acid and
nitric oxide—

$$3HNO_2 \quad = \quad HNO_3 \quad + \quad 2NO \quad + \quad H_2O.$$
Nitrous acid.   Nitric acid.   Nitric oxide.   Water.
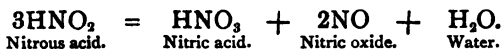
Experiment 161.—Place the residue from Exp. 156 in a flask
fitted with thistle funnel and delivery tube. Add dilute sul-
phuric acid and heat gently ; collect the evolved gas over water
in the pneumatic trough. On the admission of air the gas
turns red, showing it to consist of nitric oxide.

173. **Properties.**—This gas is colourless, but immediately, on coming in contact with air, combines with the oxygen and forms higher nitrogen oxides of a ruddy tint; from its possessing these properties it is difficult to either taste or smell it. The strong odour observed during its preparation is that of these higher oxides.

Nitric oxide is liquefied at $-11°$ C. by a pressure of 104 atmospheres. It is much more stable than nitrogen monoxide, and may be subjected to even a red heat without decomposition; consequently a lighted taper does not burn in it.

Phosphorus, when feebly ignited, is also extinguished, but if strongly ignited burns with almost as much brilliancy as in pure oxygen—

$$P_4 \quad + \quad 10NO \quad = \quad 2P_2O_5 \quad + \quad 5N_2.$$

Phosphorus.   Nitric oxide.   Phosphorus pentoxide.   Nitrogen.
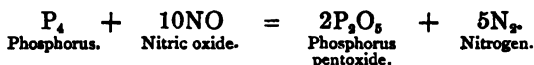
Experiment 162.—In the third jar of gas prepared introduce a lighted taper; notice that it goes out. If this is quickly done, a deflagrating spoon containing brightly burning sulphur may be placed in the same jar of gas; this also ceases to burn.

Experiment 163.—Place a piece of phosphorus in the deflagrating spoon, first thoroughly cooling it; get the second jar of gas ready, and just kindle the phosphorus and *immediately* place it in the gas; it is extinguished. Remove it and again ignite, and let it get to burn brightly; once more plunge it in the jar; it burns with extreme brightness.

A mixture of carbon disulphide vapour and nitric oxide burns with an intense bluish light.

Experiment 164.—Pour half a cubic centimetre of carbon disulphide into a test-tube; replace the bottle. Take the first jar prepared of nitric oxide, remove the cover, quickly pour in the disulphide, and as quickly re-cover the jar; shake it vigorously, in order to thoroughly mix the gas and vapour, holding the plate on firmly. Remove the plate and apply a light; the mixture burns quietly with a bright blue flame.

Nitric oxide is not itself combustible. One of its most

striking properties is the power it possesses of spontaneously combining with oxygen on the two being brought together; the resultant ruddy gas is a mixture of nitrogen trioxide and peroxide in varying proportions—

$$4NO + O_2 = 2N_2O_3, \text{ Nitrogen trioxide.}$$
$$2NO + O_2 = 2NO_2, \text{ Nitrogen peroxide.}$$
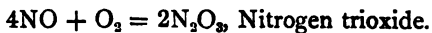
As nitrous oxide does not possess this property, this reaction serves to distinguish the one gas from the other.

Experiment 165.—Take the fourth jar of gas prepared and invert it in the pneumatic trough. Having filled a jar with oxygen, pour the nitric oxide up into it bubble by bubble; as each bubble enters, a red colour is developed; this again vanishes, and the water rises in the gas-jar. If the two gases be pure, the gradual addition of nitric oxide causes the oxygen to disappear entirely.

Prepare a jar of nitrous oxide, free from air; add nitric oxide to it in a similar manner. There is no red coloration nor rapid absorption of the gas by the water.

The reason of the above reaction is that, while nitric oxide is but feebly soluble in water (water dissolves about one-twentieth of its volume), the higher oxides produced are very soluble, and are thus absorbed as rapidly as formed. This reaction is a most important one, as the whole process of manufacturing sulphuric acid is dependent on it. A description of its employment for that purpose is given in Chapter XXI.

174. **Composition.**—The anomalous composition of nitric oxide has been already referred to in Chapter XI. From the formula being written N_2O_2 by some chemists, the name *nitrogen dioxide* has been given it, and is still used, although but one atom of oxygen is contained in the molecule. It is a general rule that the more atoms a molecule contains, the more unstable it is. Nitric oxide is more stable than nitrogen monoxide, and this, therefore, is an additional reason for considering its true formula to be NO.

175. Nitrogen Trioxide is one of the products of oxidation of nitric oxide. It dissolves in a small quantity of water to form nitrous acid. This is, however, so unstable that even the addition of more water causes its decomposition—

$$\underset{\substack{\text{Nitrous anhydride, or}\\\text{nitrogen trioxide.}}}{N_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitrous acid.}}{2HNO_2}$$

If the gas be passed into a solution of caustic potash or ammonia, it is absorbed, and a nitrite is formed—

$$\underset{\substack{\text{Nitrous}\\\text{anhydride.}}}{N_2O_3} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KHO} = \underset{\substack{\text{Potassium}\\\text{nitrite.}}}{2KNO_2} + \underset{\text{Water.}}{H_2O.}$$
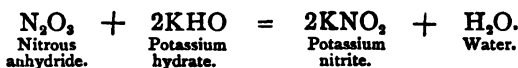
Nitrites are decomposed by stronger acids, with evolution of nitrogen trioxide—

$$\underset{\substack{\text{Potassium}\\\text{nitrite.}}}{2KNO_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3.}$$

This represents the simplest action of acids, but the nitrous acid formed also undergoes decomposition into nitric oxide, and nitric acid produced by the extra atom of oxygen uniting with another molecule of nitrous acid.

176. Nitrogen Peroxide is of but little importance. Like nitric oxide, the formula is anomalous, being NO_2. At a low temperature, however, the density increases, when N_2O_4 may be considered a true representation of the molecule.

It may be prepared by the action of heat on certain nitrates, as lead nitrate—

$$\underset{\text{Lead nitrate.}}{2Pb(NO_3)_2} = \underset{\substack{\text{Lead}\\\text{oxide.}}}{2PbO} + \underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{4NO_2} + \underset{\text{Oxygen.}}{O_2}$$
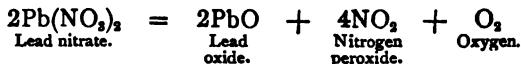
Summary.

Five oxides of nitrogen are known, two at least of which form acids.

Nitric acid is the most important; is produced by lightning

discharges. It is manufactured from nitrates by distillation with sulphuric acid. It is a powerful oxidizing agent, attacks most of the metals, but neither gold nor platinum; these may be dissolved by *aqua regia*, a mixture of hydrochloric and nitric acids. When metals are acted on by nitric acid, the lower oxides of nitrogen are evolved and nitrates formed; they are also produced by acting on metallic oxides or carbonates with the acid. The nitrates also are capable of powerful oxidizing action.

Nitrogen monoxide is usually prepared by heating ammonium nitrate. It is colourless, has a faint, sweetish odour and taste, is somewhat soluble in water, non-inflammable, supports combustion, but requires for that purpose an initial heat sufficient to start its decomposition into nitrogen and oxygen. It also acts as an anæsthetic.

Nitric oxide is prepared by the action of copper on nitric acid. It is colourless, but on exposure to air immediately becomes red by combination with oxygen. It is more stable than nitrogen monoxide, and does not support combustion unless the heat of the burning body is sufficiently intense to separate it into oxygen and nitrogen. The red fumes formed by its combination with oxygen are soluble in water. The composition of the gas is anomalous.

Nitrogen trioxide and peroxide are comparatively unimportant.

OBJECT DEMONSTRATION.

Examine samples of native potassium and sodium nitrates, the former, if procurable, as an actual incrustation of soil.

Examine and note appearance and physical characters of nitric acid and carbon disulphide.

LABORATORY DIRECTIONS.

Blocking for the adjustment of height of different pieces of apparatus is in constant requisition in the laboratory. Pieces six inches square are of a convenient size; the following thicknesses should be kept in stock : half-inch, one, two, three, and four inches.

Small pieces of gold-leaf are quite sufficient for the experiments with that substance; one leaf may be cut into nine

pieces. Do not attempt to handle the leaf in a draughty room; a leaf should be removed from the book, placed on a pad, and cut with an old knife, the edge of which is quite smooth. When the leaf is cut, it may be taken on the point of the knife and scraped into the test-tube; it may then be washed down by a few drops of water from a wash-bottle.

In adding ammonium carbonate to nitric acid, do not throw it in the form of a fine powder, as the action then is so violent that it is likely to overflow the breaker. Pieces about the size of peas are the most convenient.

The flask used for the preparation of nitrogen monoxide should not be less than 8 oz., as otherwise some of the melting nitrate may froth up and choke the tube; should any do so, immediately remove the light, as the continued evolution of gas might burst the flask. If the heat is too great, the gas comes over impure; if it is cloudy in the jar, that may be looked on as a sign that the heat must be moderated.

The action of copper on nitric acid sometimes does not start immediately; if so, apply a very gentle heat to the flask until the action commences. It is liable then to proceed with extreme rapidity; a large flask is therefore used. If coming over too fast, pour in a little water; this will render the reaction less violent. The cork and tubing used should be washed at once after use. The directions for the protection of the cork and tubing are important; if a long piece of indiarubber tubing be used, the tubing is not only destroyed, but also gets stopped with the products of corrosion. It is a good plan to have the leading tube bent out of one piece of glass tubing; but if there is a joint, provided the ends of the glass tubes touch one another, it will not matter.

The reason why the order of collection of the gas must be remembered is that that which first comes over is purer. At the last nitrogen monoxide and nitrogen are also present; the jars first filled are therefore used for those experiments in which the purest gas is required.

The phosphorus must be introduced into the gas *very quickly* when lighted, as otherwise it will be burning too brightly to be extinguished. Place the gas-jar close to the Bunsen burner, and loosen the glass plate *before* lighting the phosphorus.

CHAPTER XVIII.

SULPHUR.

Symbol, S. Atomic weight, 31·98. Density, 31·98. Specific gravity of native crystals, 2·07. Molecular weight, 63·96. Molecular volume, ▭

177. Occurrence.—Sulphur is a widely distributed element. In the neighbourhood of volcanoes it occurs plentifully in the free state. The ores from which many metals are derived are sulphides. Among these may be mentioned those of lead, copper, mercury, and zinc. Many of the native metallic sulphides are characterized by a bright metallic lustre. The most common sulphide is that of iron. From this large quantities of sulphur are extracted.

Experiment 166.—Heat a small quantity of powdered native sulphide of iron in a test-tube; yellow drops condense in the upper part of the tube.

The reaction is represented by the following equation:—

$$3FeS_2 \quad = \quad Fe_3S_4 \quad + \quad S_2$$

Ferric sulphide.   Triferric tetrasulphide.   Sulphur.

In the presence of a limited supply of air the whole of the sulphur is driven off, an oxide of iron remaining. In practice about half of the sulphur is also oxidized into sulphur dioxide, so that the yield of sulphur is not more than 50 per cent. of that present in the ore. The reaction

in this case is thus represented, the oxidation of the sulphur being omitted :—

$$4FeS_2 \; + \; 3O_2 \; = \; 2Fe_2O_3 \; + \; 4S_2.$$
Ferric sulphide.   Ferric oxide.
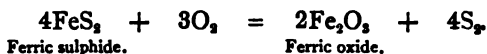
Experiment 167.—Take a piece of combustion tubing 6 inches long and one quarter-inch diameter ; place a small quantity of the sulphide about half-way up. Hold the tube slanting and apply heat ; an upward current of air is produced, in which the liberated sulphur burns. Smell the gas issuing from the end ; it has the characteristic odour of burning sulphur.

The sulphates are another important class of natural bodies containing sulphur. Of these gypsum or calcium sulphate, $CaSO_4$, and barium sulphate, $BaSO_4$, occur in large quantity.

Many organic bodies contain sulphur as an essential ingredient, especially albumin. Hence, in their putrefaction, sulphur compounds are among the products, and are always present in sewage gases, etc. White of egg is an almost pure form of albumin, and owes its odour when rotten to the presence of a compound of sulphur and hydrogen.

178. Preparation.—The free sulphur, collected in volcanic districts, is contaminated with earthy impurities. These are removed on the spot by melting the sulphur from them ; or, in the poorer samples, by the process of distillation. The crude sulphur thus obtained is further purified, on its arrival in this country, by being a second time distilled. The retorts employed are of iron ; the necks lead into large chambers of brickwork. If the heat be applied slowly, the vapour, on entering the chamber, condenses to a solid, and falls as a fine dust to its floor. This constitutes "flowers of sulphur." At a higher temperature the walls are heated, the sulphur condenses to the liquid form on them, and runs to the bottom as a melted mass. This is drawn

off into cylindrical wooden moulds and allowed to solidify. In this manner is produced the roll "brimstone" of commerce.

179. Properties.—Sulphur is a lemon-yellow solid. It is insoluble in water, and therefore possesses no taste, but has a faint odour. The rolls of sulphur are extremely brittle, and as it is also a bad conductor of heat the warmth of the hand is often sufficient to cause a roll to fall in pieces when held. It melts at a temperature of 113 C. to a limpid yellow liquid, which, if allowed to cool slowly, deposits long prismatic needle-like crystals. These are at first perfectly transparent, but after a time become opaque, through each breaking up into a number of minute rhombic octahedral crystals. The external form is still retained, but little coherence remains.

If sulphur be dissolved in carbon disulphide, and the liquid then allowed to evaporate, the sulphur is obtained in octahedral crystals of the rhombic system. These are permanent in air, and the form is that in which native sulphur crystals occur.

Experiment 168.—Take a clay crucible about 3 inches high, or, preferably, an iron ladle ; fill it with sulphur and heat very gently with a small flame, taking care that the sulphur and the flame do not come in contact. As soon as the whole of the sulphur is melted, remove the Bunsen ; as it cools, a crust forms over the surface, crystals being seen to shoot out from the side. Immediately that this crust is formed, bore two holes through with a red-hot ron wire close to the edge and opposite each other ; pour the sulphur (which still remains melted) out, and then cut round the upper crust with a knife and remove it ; the interior is one mass of long transparent needles (prisms), belonging to the oblique system. Set the mass aside for a week, and then observe that the crystals have lost their transparency.

Shake up some flowers of sulphur with carbon disulphide so as to form a saturated solution. Decant off the clear liquid and filter into an evaporating basin. Set aside and allow the disulphide to evaporate spontaneously. A residue of more or less transparent octahedra of sulphur remains.

T

There are, then, two distinct forms in which sulphur crystallizes ; the one from fusion, the other from solution. The latter are permanent, the former unstable, gradually changing into the latter.

In addition to these two varieties, there is another known as plastic sulphur, whose properties widely differ from those of either. If, instead of allowing the limpid yellow liquid, produced as a result of melting sulphur, to cool, the application of heat be continued, a remarkable series of changes ensues. The colour gradually darkens as the temperature rises ; at the same time the liquid becomes thicker, until, at a temperature of 180° C., the mass is almost black, and so viscid that the vessel may be momentarily held inverted without the sulphur running out. With a further increase of temperature, the sulphur again becomes liquid, but remains of a much thicker consistency than it possessed on first melting. If while in this state it be poured into water, a soft, indiarubber-like mass is produced, of a yellowish-brown tint, which may be drawn out into long threads. The difference between these and the common brittle form of sulphur is very striking. In a few hours it loses its tenacity, becoming again opaque and brittle. At a temperature of 446° sulphur boils.

In addition to the three forms of sulphur described, there are some other varieties, which, however, are not of great importance.

Experiment 169.—Place some sulphur in a test-tube and heat gently, until the whole has melted down into a limpid clear liquid. Pour a portion out on to an iron plate or other cold surface. It solidifies to a brittle yellow mass possessing the same properties as those originally belonging to the sulphur.

Next heat the remainder very gently, and notice the successive changes, from a thin liquid of light colour to the almost black, treacly mass. When in this condition invert the tube ; the sulphur does not run out, or only very slowly. Continue the application of heat until the sulphur boils ; observe the dark orange-coloured vapour, which condenses to solid yellow

particles in the upper part of the tube. Pour the liquid into a trough of cold water ; notice the plastic condition of the sulphur. Reserve some for a week ; it will have become brittle.

Sulphur is highly inflammable, burning in air with a pale blue flame, and emitting a suffocating odour, the reaction being represented by—

$$S_2 \quad + \quad 2O_2 \quad = \quad 2SO_2.$$

Sulphur.   Oxygen.   Sulphur dioxide.
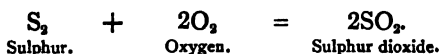
Traces of a higher oxide of sulphur are also formed, the formation of which will be subsequently described.

Sulphur also combines readily with other elements. Iron, copper, and others burn brightly when heated with it. Silver and sulphur combine at ordinary temperatures, giving the metal a black coating of silver sulphide.

Experiment 170.—Raise some sulphur to the boiling-point in a test-tube. Insert a coil of fine copper wire in the vapour— and notice the vivid combustion which ensues.

Two compounds of sulphur with hydrogen are known— SH_2 and S_2H_2—which are analogous in composition to the oxides of hydrogen, OH_2 and O_2H_2. The first of these is the only one of practical importance. The sulphides of the metals have usually corresponding formulæ to the oxides. Thus the sulphide of copper is CuS; the oxide, CuO. Sulphur in these compounds behaves as a dyad ; but in sulphuric acid and the sulphates its atomicity is VI.

Summary.

Sulphur is found native in volcanic districts, also as sulphides and sulphates, and in several organic bodies ; is purified by distillation ; is a lemon-yellow brittle solid ; occurs in two crystalline forms, one of which is unstable ; may be also obtained in the plastic form by the application of heat. It is highly inflammable, and combines with most of the metals, and also with many of the non-metals. Its absolute atomicity is VI.

OBJECT DEMONSTRATION.

Examine and note appearance of native sulphur occurring as an incrustation on igneous rocks (lava). Also examine native sulphides of iron (pyrites), copper, and lead (galena). Observe also gypsum and barytes as native sulphates, and white of egg and gluten of wheat as examples of organic bodies containing sulphur.

Examine and compare the various commercial forms of sulphur, roll sulphur, flowers of sulphur, and precipitated sulphur.

LABORATORY DIRECTIONS.

For the first experiment in this chapter the native sulphide should be used; that employed in the manufacture of sulphuric acid is most suitable. To succeed in obtaining sulphur crystals by solidification of the melted body, bore the holes through the crust *immediately* it forms, and drain the melted sulphur away *completely*.

In pouring sulphur from a test-tube, there is danger of the tube cracking unless the upper part is thoroughly heated. The safest plan is, before pouring, to boil the sulphur until the whole tube is full of uncondensed vapour; by this means the whole is uniformly heated, and the danger of cracking is but little; care should, however, be taken that the tube is so held that, in the event of its breaking, none of the sulphur should fall on the hands. The liquid will probably take fire as it leaves the test-tube; this, however, is of no importance. Should any fall on the bench, at once throw a little water on it.

CHAPTER XIX.

SULPHURETTED HYDROGEN.

Formula, SH₂. Molecular weight, 33·98. Density, 16·99 Specific gravity, 1·1912.

Formula, SH_2. Molecular weight, 33·98. Density, 16·99 Specific gravity, 1·1912.

Graphic formula, $H-S-H$.
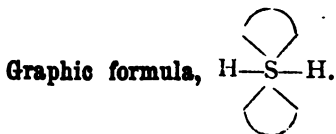
180. **Occurrence.**— This compound, which is also sometimes known by the name of hydrosulphuric acid, is found free in volcanic districts, and also in the waters of certain mineral springs, as those at Harrogate.

181. **Preparation.**—It is formed when hydrogen is passed into sulphur vapour, but only in small quantities—

$$S_2 \quad + \quad 2H_2 \quad = \quad 2SH_2.$$
Sulphur. Hydrogen. Sulphuretted hydrogen.

Experiment 171.—Arrange a small retort with its stem just dipping beneath the surface of the water in a pneumatic trough. Place some sulphur in the retort and heat to the boiling-point ; notice the sulphur which condenses in the stem. Withdraw the stopper from the tubulure of the retort, and insert a cork through which has been passed a glass tube of such a length as to reach almost to the surface of the melted sulphur. Through this tube pass some pure hydrogen gas, and collect it as it escapes from the stem of the retort. The gas possesses the odour of putrid eggs, and a piece of paper moistened with a solution of lead acetate is blackened when plunged into the gas.

Sulphuretted hydrogen is commonly prepared for use in the laboratory by the action of dilute sulphuric acid on a sulphide, that of iron being usually chosen.   The reaction goes on readily, without the application of heat, the iron displacing the hydrogen, and the sulphur and hydrogen uniting—

$$\underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{\text{FeS}} \quad + \quad \underset{\text{Sulphuric acid.}}{\text{H}_2\text{SO}_4} \quad = \quad \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{\text{FeSO}_4} \quad + \quad \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{\text{SH}_2.}$$
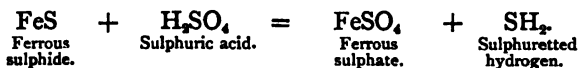
Experiment 172.—Fit up the apparatus used for the preparation of hydrogen, attach a small flask as a wash-bottle (Fig. 49), and place in it a little water ; place in the flask some fragments of iron sulphide ; add 3 or 4 oz. of water, and then a *small* quantity of sulphuric acid ; the gas is rapidly evolved.   Fill three jars with it over warm water

Experiment 173.—In the next place, attach a jet to the generating apparatus and light the gas ; it burns with a feeble blue flame, producing water and sulphur dioxide.   Hold just above the flame a rod which has been dipped in a strong solution of ammonia (ammonium hydrate) ; dense white fumes ascend.

The combustion of sulphuretted hydrogen is represented by the equation—

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{\text{SH}_2} \quad + \quad \underset{\text{Oxygen.}}{3\text{O}_2} \quad = \quad \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2\text{SO}_2} \quad + \quad \underset{\text{Water.}}{2\text{H}_2\text{O.}}$$
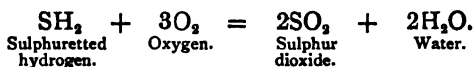
On holding above the flame the rod dipped in ammonia, the sulphur dioxide forms a solid compound named ammonium sulphite.   The fumes of this body are evidence of the presence of sulphur dioxide—

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{\text{SO}_2} \quad + \quad \underset{\substack{\text{Ammonium}\\\text{hydrate.}}}{2\text{NH}_4\text{HO}} \quad = \quad \underset{\substack{\text{Ammonium}\\\text{sulphite.}}}{(\text{NH}_4)_2\text{SO}_3} \quad + \quad \underset{\text{Water.}}{\text{H}_2\text{O}}$$
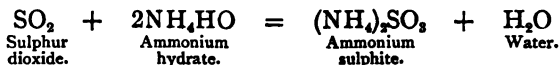
Sulphuretted hydrogen produces no fumes with ammonia. More conclusive evidence of the presence of sulphur dioxide as one of the products of combustion is afforded by holding the nose above the flame, when its characteristic odour is

observed. The following experiment also illustrates a test frequently employed for the detection of sulphur dioxide :—

Experiment 174.—Hold over the flame a piece of filter paper which has been dipped in a mixture of potassium chromate and dilute hydrochloric acid ; the yellow colour is changed to green by the reducing action of the sulphur dioxide.

Prove also that water is produced when sulphuretted hydrogen burns, by holding a beaker of cold water in the flame ; moisture condenses on the cold surface.

Sulphuretted hydrogen is soluble in cold water, one volume at 15° C. dissolving 3·23 volumes of the gas.

Experiment 175.—At the conclusion of the experiment with flame pass the gas into a little distilled water in a test-glass or beaker ; the arrangement of the apparatus is shown in Fig. 49. If necessary, add a little more sulphuric acid to the ferrous sulphide in flask A. Continue the passage of the gas for about ten minutes, and then notice that the water has the odour of the gas.
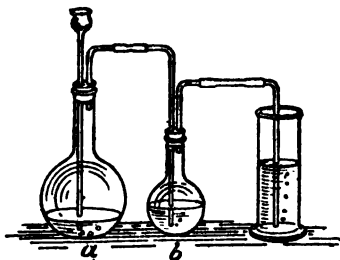
While the above experiment is proceeding, examine the three jars filled with the gas in the following manner :—

FIG. 49.—Preparation of sulphuretted hydrogen.

Experiment 176.—Remove the cover from one jar, and introduce a lighted taper ; the gas burns, but the light is extinguished ; a yellow deposit of sulphur is formed on the sides of the jar.

Experiment 177.—Add some litmus solution to the second jar of gas, and shake up ; the colour of the litmus is changed to a port-wine tint, showing that the gas has feebly acid properties.

Experiment 178.—Prepare a jar of chlorine, invert it, with the plate on the mouth, over the third jar of sulphuretted hydrogen ; pull out the two plates, and the jars open into one

another; sulphur is deposited. Remove the upper jar, and notice the characteristic fumes of hydrochloric acid.

182. Properties.—The preceding experiments illustrate several of the properties of this gas. It is colourless, and has an odour of rotten eggs. Its solution in water has a corresponding taste. It is inflammable and a non-supporter of combustion. With excess of oxygen, sulphur dioxide and water are produced, according to the equation before given. When the supply of air is limited, as when the gas burns in a jar, the sulphur is in great part deposited, the hydrogen only being burned—

$$2SH_2 \quad + \quad O_2 \quad = \quad S \quad + \quad 2H_2O.$$
Sulphuretted hydrogen. Oxygen. Sulphur. Water.

The gas is condensed to a liquid by a pressure of seventeen atmospheres at ordinary temperatures.

183. Composition.—The molecule of the gas being represented by the formula SH_2, it is evident that it contains its own volume of hydrogen. Its composition may be proved by heating metallic tin in it. When cold the gas is found to have regained its original volume and to consist of hydrogen. A piece of paper dipped in a solution of lead acetate is not changed in colour by the residual gas, although it is immediately blackened by sulphuretted hydrogen. The sulphur and tin have combined to form stannous sulphide—

$$SH_2 \quad + \quad Sn \quad = \quad SnS \quad + \quad H_2.$$
Sulphuretted hydrogen. Tin. Stannous sulphide. Hydrogen.
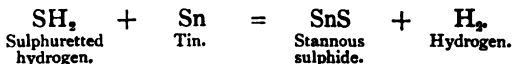
The experiment may be performed in the following manner :—

Experiment 179.—First close the end of a piece of combustion tubing, 8 or 10 inches in length, blowing it out into a small bulb ; bend it over, about 2 inches from the end, to an acute angle. Place a few fragments of granulated tin in the closed end ; fill with sulphuretted hydrogen by displacement, and then

invert in a small trough of mercury. The mercury should stand in the tube some distance from the bottom ; some of the gas may therefore be allowed to escape by holding the tube over at an angle, its mouth being kept the whole of the time under the surface of the mercury. Clamp the tube with a holder, and apply heat very carefully ; the sulphur and tin combine. Allow to cool, and observe the volume. Before heating, an india-rubber ring should be slipped over the tube to mark the level of the gas.

184. **Acidity of Sulphuretted Hydrogen.**—The action of sulphuretted hydrogen on litmus shows that the gas possesses acid properties. These are, however, so feeble that in the case of soluble sulphides carbon dioxide is able to displace the sulphuretted hydrogen. The sulphides of all the metals are insoluble in water, with the exception of those of calcium, barium, strontium, magnesium, sodium, and potassium, and a few of the very rare metals. The insolubility of the other metallic sulphides affords to the analyst a very valuable means of separating those metals from the group above mentioned. Whenever two compounds are brought together which respectively contain elements that by their union are capable of forming an insoluble compound, that compound will usually be produced; so that, although sulphuretted hydrogen is a weak acid, it is thus able to displace stronger ones from many metals. A current of sulphuretted hydrogen passed through a solution of copper chloride precipitates copper sulphide ; thus—

$$CuCl_2 \quad + \quad H_2S \quad = \quad CuS \quad + \quad 2HCl.$$
Copper chloride.   Sulphuretted hydrogen.   Copper sulphide.   Hydrochloric acid.
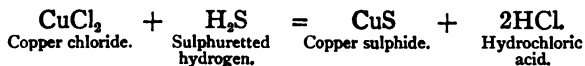
And this although hydrochloric acid is so much more powerful in its properties.

These sulphides have, in many cases, characteristic colours, by which they are immediately recognized. They possess the further advantage of being divided into two

groups, one of which is soluble in dilute hydrochloric acid, the other not so.

Experiment 180.—Prepare a solution in separate test-tubes of each of the following substances : Arsenious anhydride, copper sulphate, lead acetate, tartar emetic or antimony chloride, zinc sulphate, and ferrous sulphate. Add a few drops of hydrochloric acid to each, and pass sulphuretted hydrogen through each solution from the generating apparatus, washing the leading tube between each solution.

The following results are observed :—

$$As_2O_3 + 3SH_2 = 3H_2O + As_2S_3, \text{ Lemon Yellow.}$$
<div align="left">Arsenious anhydride.</div> <div align="right">Arsenious sulphide.</div>

$$CuSO_4 + SH_2 = H_2SO_4 + CuS, \text{ Black.}$$
Copper sulphate.   Copper sulphide.

$$Pb(C_2H_3O_2)_2 + SH_2 = 2HC_2H_3O_2 + PbS, \text{ Black.}$$
Lead acetate.   Acetic acid.   Lead sulphide.

$$2SbCl_3 + 3SH_2 = 6HCl + Sb_2S_3, \text{ Orange.}$$
Antimony chloride.   Antimony sulphide.
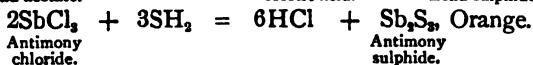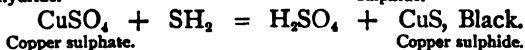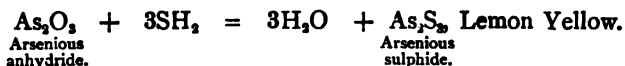
$ZnSO_4$, Zinc sulphate $\left.\right\}$ In acid solution, SH_2 produces no
$FeSO_4$, Iron sulphate $\left.\right\}$ precipitate.

Through fresh portions of zinc and iron sulphates, *without* the addition of hydrochloric acid, pass sulphuretted hydrogen—

$$ZnSO_4 + SH_2 = H_2SO_4 + ZnS, \text{ White.}$$
Zinc sulphate.   Zinc sulphide.

$$FeSO_4 + SH_2 = H_2SO_4 + FeS, \text{ Black.}$$
Iron sulphate.   Iron sulphide.
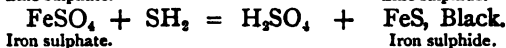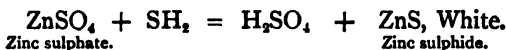
To these two now add a few drops of hydrochloric acid ; the precipitates are immediately redissolved.

The sulphides are shown by these experiments to be well-defined salts, and a series of bodies of great importance.

Although sulphur is thus able to displace the metals from their compounds with chlorine, owing to the operation of the law previously mentioned, yet chlorine readily decomposes sulphuretted hydrogen, as shown by experiment, the action being—

$$2SH_2 + 2Cl_2 = S_2 + 4HCl.$$
Sulphuretted hydrogen.   Chlorine.   Sulphur.   Hydrochloric acid.
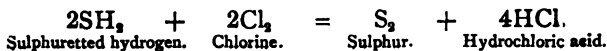
185. Decompositions of Sulphuretted Hydrogen.—The great affinity of hydrogen and chlorine for each other causes the decomposition of the sulphuretted hydrogen, as shown in the equation given at the close of the last paragraph.

Free oxygen has no action on the dry gas, but in the presence of water a slow oxidation takes place. Hence an aqueous solution of sulphuretted hydrogen becomes turbid on exposure to the atmosphere, through the separation of sulphur and the formation of water—

$$2SH_2 \quad + \quad O_2 \quad = \quad S_2 \quad + \quad 2H_2O.$$
Sulphuretted hydrogen.   Oxygen.   Sulphur.   Water.
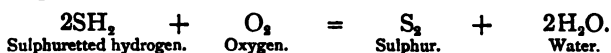
A curious and interesting reaction takes place between sulphuretted hydrogen and sulphur dioxide when moist; on bringing together the mouths of two jars containing these gases, they decompose each other with the separation of sulphur and formation of water. Apparently the decomposition is in part determined by the affinity of the sulphur atoms for each other, in the same way as the affinity of oxygen atoms causes the mutual decomposition of hydroxyl and silver oxide. In the above reaction an acid of sulphur known as pentathionic acid is also formed—

$$10SO_2 \quad + \quad 10SH_2 \quad = \quad 5S_2 \quad + \quad 8H_2O \quad + \quad 2H_2S_5O_6.$$
Sulphur dioxide.   Sulphuretted hydrogen.   Sulphur.   Water.   Pentathionic acid.
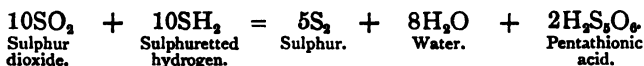
This reaction is of interest as being that by which probably much of native sulphur has been deposited, both of these gases being emitted from volcanoes.

Under sulphur dioxide, directions are given for the performance of this experiment.

Summary.

Sulphuretted hydrogen occurs free in the gases evolved from volcanoes. May be prepared by passing hydrogen into sulphur vapour; also by the action of sulphuric acid on sulphides. It burns in excess of air to sulphur dioxide and water; with less air sulphur is deposited. The sulphur dioxide produced by its

burning may be recognized by its action with ammonia, and also on a mixture of potassium chromate and hydrochloric acid. Sulphuretted hydrogen is soluble in water; is colourless, and has a disgusting odour of rotten eggs; is a non-supporter of combustion. By the action of chlorine it is decomposed. A given volume of the gas contains its own volume of hydrogen; its composition is determined by heating it with metallic tin. It possesses feeble acid properties; certain sulphides possess characteristic colours by which they may be recognized.

Sulphuretted hydrogen is also decomposed by sulphur dioxide.

LABORATORY DIRECTIONS.

After the preparation of sulphuretted hydrogen, wash out the apparatus before it is put away; otherwise a mass of crystal of iron sulphate may form. Any remaining iron sulphide should be washed, and returned, when dry, to the jar. There is sometimes some difficulty, when sulphide is taken which has been before used, in getting the action to commence; there should always be a little new sulphide added as well. The difficulty sometimes arises through the acid being too strong.

In Exp. 179 take care that the tin is not allowed to drop into the mercury. The application of heat should be continued for some time.

CHAPTER XX.

OXIDES OF SULPHUR.

THREE oxides of sulphur are known :—

Sulphur sesquioxide, S_2O_3.

Sulphur dioxide or sulphurous anhydride, SO_2.

Sulphur trioxide or sulphuric anhydride, SO_3.

The latter two of these only will be considered in this work.

SULPHUR DIOXIDE AND SULPHUROUS ACID.

Sulphur Dioxide. — Formula, SO_2. **Molecular weight, 63·9. Density, 31·95. Specific gravity, 2·247.**

Graphic formula,
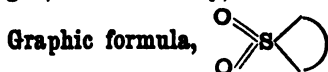
186. **Occurrence.**—This compound is a gas at ordinary temperatures, and is emitted in vast quantities from volcanoes. The student is already familiar with its preparation by the combustion of sulphur in oxygen.

187. **Preparation.**—When required for laboratory use it is prepared by the action of some deoxidizing agent on sulphuric acid.

It has already been shown that zinc energetically displaces the hydrogen from sulphuric acid ; but certain other metals, as copper, silver, and mercury, are without action, except on the application of heat, when chemical action ensues, which is probably represented by the following equation :—

$$Cu \quad + \quad H_2SO_4 \quad = \quad CuSO_4 \quad + \quad 2H.$$

Copper.   Sulphuric acid.   Copper sulphate.   *Nascent* hydrogen
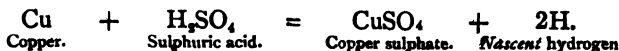
At the high temperature the nascent hydrogen attacks a second molecule of sulphuric acid ; thus :—

$$2H \quad + \quad H_2SO_4 \quad = \quad 2H_2O \quad + \quad SO_2.$$
Nascent hydrogen.   Sulphuric acid.   Water.   Sulphur dioxide.
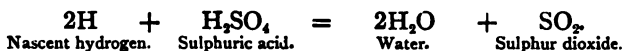
These successive steps in the reaction may be grouped together in one equation—

$$Cu \quad + \quad 2H_2SO_4 \quad = \quad 2H_2O \quad + \quad CuSO_4 \quad + \quad SO_2.$$
Copper.   Sulphuric acid.   Water.   Copper sulphate.   Sulphur dioxide.

Sulphur dioxide may also be prepared from sulphuric acid by the action of charcoal ; carbon dioxide, however, is also produced—

$$2H_2SO_4 \quad + \quad C \quad = \quad 2SO_2 \quad + \quad CO_2 \quad + \quad 2H_2O.$$
Sulphuric acid.   Carbon.   Sulphur dioxide.   Carbon dioxide.   Water.

The gas, being soluble in water, must be collected by displacement or over mercury. For the purpose of testing the properties of the gas, prepare three jars in the following manner :—

Experiment 181 — Fit up the generating apparatus shown in Fig. 50, put in about half an ounce of copper turnings or strips, set the flask on a tripod or retort stand, pour in 3 oz. of strong commercial sulphuric acid, and apply heat. After a time, as the temperature increases, the liquid in the flask effervesces, and sulphur dioxide is evolved ; collect by downward displacement. To determine when the jar is full, hold

FIG. 50. – Preparation of sulphur dioxide.

a match near its mouth ; the gas extinguishes it. As soon as

the action commences, the flame may be lowered. The jars and plates used must be quite dry

188. Properties.—At a temperature of $-8°$ C. sulphur dioxide condenses to a colourless liquid, which freezes at $-76°$ C.; at $15°$ C. the gas condenses with a pressure of $2\frac{1}{2}$ atmospheres.

Experiment 182.—Dry the gas evolved from the generating apparatus by passing it through concentrated sulphuric acid in a small wash-bottle; next pass it through a spiral glass, or pewter, worm, enclosed in a vessel containing a mixture of ice and salt. Let the end of the spiral dip into a test-tube, which is also placed in some of the ice and salt mixture; as the gas
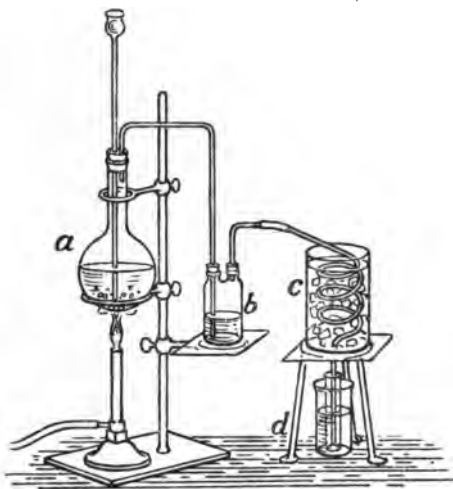
FIG. 51.—Liquefaction of sulphur dioxide.

passes through the worm it is condensed, and collects in the test-tube. When a little of the liquid has accumulated, pour it on the bulb of an alcohol thermometer, around which cotton-wool has been wrapped; notice the great cold produced by the rapid evaporation. The gas may be retained in the liquid form by hermetically sealing the tube containing it; the upper end

may be softened and drawn off by the blowpipe while the tube remains in the freezing mixture.

Fig. 51 represents a form of the apparatus : *a* is the generating flask, *b* the wash-bottle, *c* the condensing worm, and *d* the small bottle, or test-tube, in which the liquefied gas is collected.

Experiment 183.—In one of the jars of gas place a burning taper ; it is immediately extinguished, and the gas does not take fire. In the same bottle pour a little litmus solution, and shake up ; the colour changes to red, and in a little while disappears.

Experiment 184.—Open the second jar under water in the trough ; the water rushes up and fills the jar. Pass some of the gas, after washing in a very small wash-bottle containing a layer of about half an inch of water, into a little distilled water in a beaker, in the same way as sulphuretted hydrogen was obtained in solution; notice that the gas is almost entirely dissolved, and that the liquid acquires the taste and smell of the gas.

Experiment 185.—Hold over the jet from which the gas is issuing a piece of paper dipped in a mixture of a solution of potassium chromate and hydrochloric acid ; the colour is changed from yellow to green. This is a convenient test for the presence of sulphur dioxide.

Experiment 186.—Prepare a jar of sulphuretted hydrogen, and place on it the remaining jar of sulphur dioxide ; remove the plates; observe that sulphur is deposited. The reaction was described with an equation in the last chapter.

From experiments the student has seen that sulphur dioxide is a colourless gas with a strong pungent odour; when diluted with air, coughing and sneezing are produced by it ; in a concentrated form it causes suffocation. Water at a temperature of 15° C. dissolves 47 volumes of this gas ; the solution thus produced contains a true acid, sulphurous acid, H_2SO_3, which separates out in cubical crystals at 0° C. ; this is decomposed at a higher temperature, sulphur dioxide

escapes, and water remains ; the whole of the gas may be expelled from water by boiling—

$$SO_2 \quad + \quad H_2O \quad = \quad H_2SO_3.$$

Sulphurous anhydride.   Water.   Sulphurous acid.

Experiment 187.—Add to some of the sulphurous acid previously made some barium chloride solution ; a white precipitate of barium sulphite is formed —

$$H_2SO_3 \quad + \quad BaCl_2 \quad = \quad BaSO_3 \quad + \quad 2HCl.$$

Sulphurous acid.   Barium chloride.   Barium sulphite.   Hydrochloric acid.
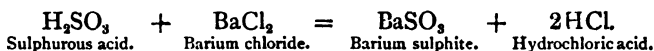
To this add a little pure dilute hydrochloric acid ; the precipitate immediately dissolves.

Place some of the solution away in a beaker or evaporating basin for a week, then add to it some barium chloride and hydrochloric acid ; the white precipitate which first formed does not probably entirely dissolve.

Like other gases which readily condense, sulphur dioxide does not implicitly follow Boyle's law (p. 38) ; the pressure being doubled, the volume contracts to less than one-half.

The gas is neither inflammable nor a supporter of combustion.

189. Bleaching Action.—The action of sulphur dioxide on litmus shows its acidity when in solution ; the further action by means of which it discharges the colour indicates that it possesses bleaching properties. As a bleaching agent it differs remarkably from chlorine ; it will be remembered that the latter decomposes water, seizing the hydrogen, and that the nascent oxygen destroys the colouring matter by change into bodies containing a larger proportion of that element.

Colouring matters which have been acted on by chlorine are entirely destroyed, and cannot be reproduced ; colours removed by sulphur dioxide are again restored either by its displacement by a stronger acid, as dilute sulphuric, or its neutralization by combination with an alkali. Miller considers the acid to act by forming colourless compounds

with the colouring matters. The action is also explained by stating that the colouring matters are reduced, the sulphurous acid being oxidized into sulphuric; it is difficult, however, with this assumption, to explain how the addition of either sulphuric acid or an alkali should again restore the colour, as neither of these bodies is an oxidizing agent. Sulphur dioxide is used for the bleaching of articles, such as silk, straw, and wool, which would be injured by the action of chlorine.

Experiment 188.—Suspend in the upper part of a deflagrating jar a bunch of red roses, or other coloured flowers; stand the jar on a dish, over a small spoon or iron plate containing some burning sulphur; the sulphur dioxide, as formed, discharges the colour. Next dip the flowers in water acidulated with sulphuric acid; the colour is restored.

In the absence of freshly gathered flowers an infusion of red roses may be employed, and some of the sulphurous acid made in a former experiment added to it.

Sulphur dioxide is used for the purpose of removing traces of chlorine from goods bleached by that agent; sulphuric and hydrochloric acids are formed by their mutual action, and may be afterwards removed by copious washing; more usually, however, the sodium salt of sulphurous acid is employed: this possesses the advantage that the alkaline base combines with the resulting acids and forms non-corrosive salts.

From its possessing this property, sodium sulphite is known commercially under the name of antichlor. Its action is represented in the following equation, where it is assumed that excess of the sulphite is used :—

$$2Na_2SO_3 \quad + \quad Cl_2 \quad = \quad Na_2SO_4 \quad + \quad 2NaCl \quad + \quad SO_2.$$

| Sodium sulphite. | Chlorine. | Sodium sulphate. | Sodium chloride. | Sulphur dioxide. |

190. Composition.—As the molecule of sulphur dioxide contains two atoms of oxygen, it yields on decomposition its own volume of that gas; or, on burning sulphur

in oxygen over mercury, the volume of the gas remains unaltered; from the atomic weight of sulphur being (very nearly) double that of oxygen, the molecular weight of sulphur dioxide is also double that of oxygen.

191. Sulphurous Acid.—Sulphurous acid is dibasic, and forms two series of salts called sulphites : these are all decomposed by the action of a stronger acid, as sulphuric—

$$Na_2SO_3 \;+\; H_2SO_4 \;=\; Na_2SO_4 \;+\; SO_2 \;+\; H_2O.$$

Sodium sulphite. Sulphuric acid. Sodium sulphate. Sulphur dioxide. Water.
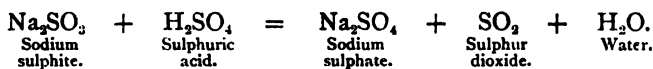
Summary.

Sulphur dioxide is emitted from volcanoes, is prepared by burning sulphur in air or oxygen, and by action of copper or carbon on sulphuric acid. The gas has a pungent odour, is colourless, possesses a characteristic taste, and may be condensed to a liquid by either cold or pressure. It is very soluble in water; the solution is acid to litmus, and contains a true acid, forming a series of salts known as sulphites.

Sulphurous acid acts as a bleaching agent; the colour, however, is re.tored by either the action of very dilute acid or an alkali. •

LABORATORY DIRECTIONS.

In inserting copper strips in a flask, take care that they do not drop through the bottom; the best plan is to hold the flask in a horizontal position and slide them in.

In heating sulphuric acid, take every precaution to prevent the cracking of the flask; for instance, do not let the flame play direct on the glass. · Never hold the hands where there is any danger, in event of a breakage, of the hot acid running on them. Should such a misfortune, by any accident, happen, *immediately* place the burned part under a copious stream of water from the tap. If sulphuric acid is spilled over the woodwork of the bench, strew over it some whiting, and when the action is over let the whole be cleaned up with sawdust.

To make a freezing mixture, pound together in a mortar two

parts of ice and one of salt; scrape this into the vessel containing the condensing worm for the condensation of sulphur dioxide. If such a condenser has to be fitted up, a deflagrating jar turned bottom upwards answers very well for the outer vessel; the mouth should be fitted with a cork, through which the end of the condensing spiral is passed. A worm made of pewter possesses the advantage of being unbreakable.

Should it be desired to preserve a sample in the liquid state, a tube of stouter glass than a test-tube must be employed; it should be drawn out at the neck before being filled, so that the final sealing may be done more quickly. Take care, however, not to draw out the neck so narrow as to prevent the tube from the end of the condenser passing in.

CHAPTER XXI.

SULPHUR TRIOXIDE AND SULPHURIC ACID.

Sulphur Trioxide.—Formula, SO_3. **Molecular weight, 79·86. Density, 39·93.**

Graphic formula, $O = S \overset{\displaystyle O}{\underset{\displaystyle O}{\Big\Vert}}$

192. Preparation.—Sulphur does not readily combine with more than two atoms of oxygen; but by passing a mixture of sulphur dioxide and oxygen over ignited spongy platinum, sulphur trioxide is produced—

$$2SO_2 \quad + \quad O_2 \quad = \quad 2SO_3.$$

Sulphur dioxide.   Oxygen.   Sulphur trioxide.
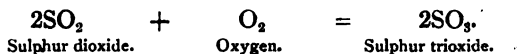
Experiment 189.—Fit up a 4-oz. flask as a wash-bottle, and one-third fill it with a saturated solution of sulphurous acid in water. Attach to the long tube in the flask an oxygen generating apparatus (either a small flask or test-tube). Blow a bulb in the centre of a piece of combustion tubing about 9 inches long; draw off one end to the size of a piece of quill tubing, and fit a cork and leading tube to the other end. Take some asbestos and soak in a solution of platinum chloride; dry it and ignite in a small crucible over the Bunsen; the chlorine is driven off, and a finely divided coating of platinum remains on the asbestos. Introduce this into the bulb of the tube, and connect up the whole by indiarubber tubing, as shown in Fig. 52. Heat the oxygen tube; the gas, in bubbling through the sulphurous acid, disengages some sulphur dioxide; a mixture of the two emerges and passes through the bulb tube.

Now heat the bulb containing the platinized asbestos; white fumes of sulphur trioxide issue from the tube; convey these by means of a piece of glass tubing, attached with indiarubber,
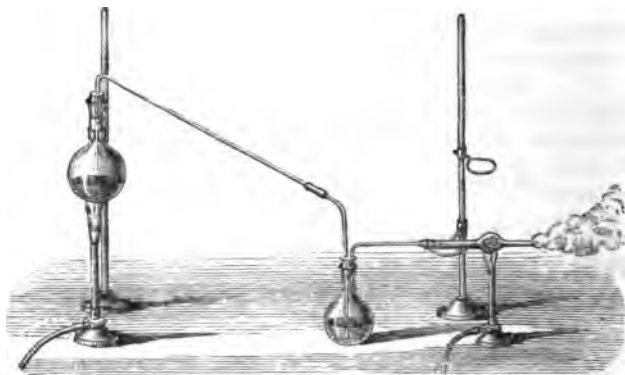
FIG. 52.—Preparation of sulphur trioxide.

into some distilled water in a small beaker. Add to the water some pure hydrochloric acid and barium chloride; an insoluble precipitate is formed.

Sulphur trioxide is also produced by the action of heat on Nordhausen sulphuric acid; thus—

$$H_2S_2O_7 \quad = \quad H_2SO_4 \quad + \quad SO_3.$$

Nordhausen   Sulphuric   Sulphur
sulphuric acid.   acid.   trioxide.
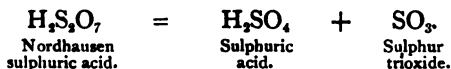
193. Properties.—Sulphur trioxide, as obtained by either of the methods above given, is a white silky-looking mass, which, when purified by repeated distillations in hermetrically sealed tubes, is changed into a colourless liquid. It is devoid of all acid properties, and may be rolled between the *dry* fingers without injury. By passage through a red-hot tube, it is separated into oxygen and sulphur dioxide—

$$2SO_3 \quad = \quad 2SO_2 \quad + \quad O_2.$$

Sulphur trioxide.   Sulphur dioxide.   Oxygen.
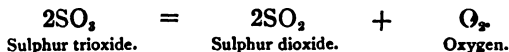
Sulphur trioxide is very deliquescent, and, when dropped

into water, dissolves with a hissing noise and evolution of great heat, forming sulphuric acid—

$$SO_3 \quad + \quad H_2O \quad = \quad H_2SO_4.$$

Sulphur trioxide, or sulphuric anhydride.   Water.   Sulphuric acid.
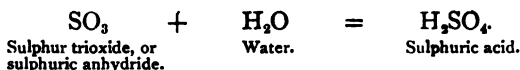
When the two are once united, their separation cannot be effected by heat alone; for a temperature sufficiently high to dissociate them also decomposes sulphur trioxide into sulphur dioxide and oxygen.

Sulphuric Acid.—Formula, H_2SO_4. **Molecular weight, 97·82. Specific gravity of liquid, 1·846. Melting-point, 10·5° C. Boiling-point, 338°.**

194. Importance.—There is no other compound, with the exception of water, which is of such importance to the chemist as sulphuric acid. The frequency of its application to various purposes in the preceding chapters will have given the student some idea of its usefulness, and have rendered him familiar with its appearance, many of its properties, and its composition. It holds an equally important position in the chemical manufactures as in the laboratory. Its preparation is the starting-point in the manufacture of hydrochloric acid, sodium carbonate, nitric acid, and many other bodies of value in the arts.

195. Preparation.—Sulphurous acid, when exposed to the atmosphere, is gradually oxidized to sulphuric acid, as was proved by an experiment described in the preceding chapter, where directions are given for some sulphurous acid to be left in an open evaporating basin for a week. A solution of barium chloride is employed as a test for sulphuric acid, with which it forms a white precipitate, insoluble in acids—

$$H_2SO_4 \quad + \quad BaCl_2 \quad = \quad BaSO_4 \quad + \quad 2HCl.$$

Sulphuric acid.   Barium chloride.   Barium sulphate.   Hydrochloric acid.
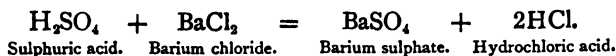
The same precipitate is formed when barium chloride is

added to a solution of a soluble sulphate. Barium chloride also produces a precipitate with sulphurous acid, which is, however, soluble in hydrochloric acid. In this way the two acids are distinguished from each other, and sulphuric acid detected in the other's presence.

The change of sulphurous into sulphuric acid is produced more rapidly by the aid of oxidizing agents.

Experiment 190.—To a little sulphurous acid, free from sulphuric acid, add a few drops of pure concentrated nitric acid ; heat gently in a test-tube ; add some hydrochloric acid and barium chloride : a white precipitate of barium sulphate is formed.

The action of the nitric acid is thus represented :—

$$H_2SO_3 \ + \ 2HNO_3 \ = \ H_2SO_4 \ + \ 2NO_2 \ + \ H_2O.$$

| Sulphurous acid. | Nitric acid. | Sulphuric acid. | Nitrogen peroxide. | Water. |
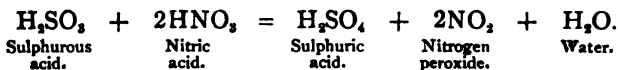
196. Composition of Acids.—Sulphurous acid may be also oxidized by the action of hydroxyl. This reaction is of some theoretical importance, as many chemists view the acids as a class of bodies in which the hydrogen exists as semi-molecules of hydroxyl. Frankland, to whom we are indebted for a systematic nomenclature which indicates the constitution of bodies, writes the formula of sulphuric acid, SO_2Ho_2. Ho is here used to represent the semi-molecule of hydroxyl, the small 2 qualifying both the hydrogen and oxygen. The same formula is conveniently written $SO_2(HO)_2$. The constitution of oxy-acids is represented, according to this theory, by the following graphic formulæ :—

| Sulphuric acid. | Sulphurous acid. | Nitric acid. |
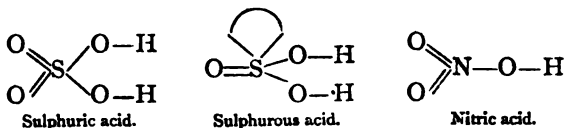
The peculiar interest of the oxidation of sulphur dioxide into sulphuric acid by hydroxyl depends on the fact that it

may be regarded as an instance of direct union between the two compounds; thus :—

$$SO_2 \quad + \quad H_2O_2 \quad = \quad SO_2(HO)_2.$$
Sulphur dioxide.   Hydroxyl.   Sulphuric acid.

The reaction may also be expressed by an equation in which sulphurous acid is oxidized by the second atom of oxygen in hydroxyl—

$$H_2SO_3 \quad + \quad H_2O_2 \quad = \quad H_2SO_4 \quad + \quad H_2O.$$
Sulphurous acid.   Hydroxyl.   Sulphuric acid.   Water.
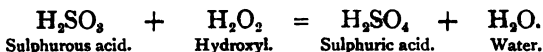
197. Direct Oxidation of Sulphur.—Sulphur itself, when moistened, is in part gradually oxidized into sulphuric acid; by prolonged boiling with nitric acid, the whole becomes oxidized.

$$S_2 \quad + \quad 12HNO_3 \quad = \quad 2H_2SO_4 \quad + \quad 12NO_2 \quad + \quad 4H_2O.$$
Sulphur.   Nitric acid.   Sulphuric acid.   Nitrogen peroxide.   Water.
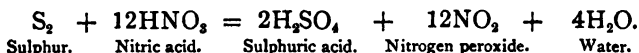
Nitric acid has a similar action on some native sulphides.

198. Manufacture.—Sulphuric acid is always manufactured on the large scale by the oxidation of sulphur dioxide in the presence of water. The reactions involved are of great interest. The vapour of nitric acid is passed into a chamber with sulphur dioxide, air, and steam. As shown in a previous experiment, the nitric acid is deoxidized into nitrogen peroxide, with the formation of sulphuric acid. A reaction now ensues between the nitrogen peroxide and some more sulphur dioxide, more sulphuric acid is produced, and the nitrogen peroxide is reduced to nitrogen dioxide. The student will remember that in the presence of air this colourless gas is immediately changed into the ruddy fumes of the trioxide and peroxide. Thus, higher oxides of nitrogen are again formed, and are capable of oxidizing more sulphur dioxide. Sulphur dioxide does not readily combine with oxygen, but is immediately oxidized by nitrogen peroxide. The dioxide unites directly with oxygen, and so acts as a carrier of oxygen from the air to

the sulphur dioxide. A small amount of nitric acid is thus theoretically capable of producing an indefinite quantity of sulphuric acid. The whole series of changes is shown in the following equations :—

$$SO_2 \; + \; 2HNO_3 \; = \; H_2SO_4 \; + \; 2NO_2.$$
Sulphur dioxide.   Nitric acid.   Sulphuric acid.   Nitrogen peroxide.

$$SO_2 \; + \; NO_2 \; + \; H_2O \; = \; H_2SO_4 \; + \; NO.$$
Sulphur dioxid.   Nitrogen peroxide.   Water.   Sulphuric acid.   Nitrogen dioxide.

$$8NO \; + \; 3O_2 \; = \; 2N_2O_3 \; + \; 4NO_2.$$
Nitrogen dioxide.   Oxygen.   Nitrogen trioxide.   Nitrogen peroxide.
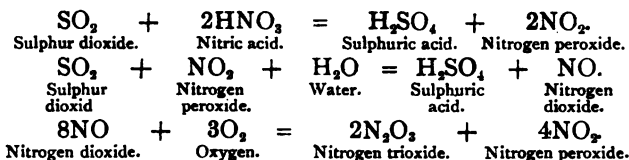
The proportions of higher oxides are not constant, but depend on the quantity of oxygen present.

The above equations represent, in the simplest form, the action which takes place. In the absence of water, a peculiar crystalline compound is produced, which may be represented by the formula $S_2O_5(NO_2)_2$. This is immediately decomposed by water, with the formation of sulphuric acid and liberation of nitrogen trioxide :—

$$S_2O_5(NO_2)_2 \; + \; 2H_2O \; = \; 2H_2SO_4 \; + \; N_2O_3.$$
Crystalline compound.   Water.   Sulphuric acid.   Nitrogen trioxide.
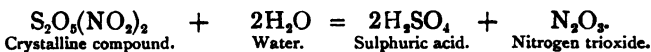
Experiment 191.—In order to study the reactions above explained, fit up the following apparatus : To a dry 32-oz. flask fit a cork, through which bore five holes, and pass through each a piece of glass tubing bent at right angles, four of which reach to about the middle of the flask ; to these attach respectively, by indiarubber tubing, an apparatus for the generation of nitrogen dioxide, another evolving sulphur dioxide, a bag containing air, with a weight on the top, and a flask for the production of steam. Through the fifth hole a tube is passed, which just enters the flask. This is provided for the escape of the waste gases ; it should be larger than the others, and have a tube leading from it into a flue or stink-cupboard. Instead of having generating flasks for the sulphur and nitrogen oxides, it is a far more convenient plan to prepare these gases previously, and store them in little gas-holders or bladders ; a dry bullock's bladder, through the neck of which a glass tube is passed, answers very well for the sulphur dioxide ; the nitric oxide may be kept in a little gas-holder over water. A screw

tap should be placed on the indiarubber tubing connecting each of these to the flask. If this form of the apparatus is used, the student's attention is not required in watching and regulating the evolution of the gases, but instead he can observe minutely the reactions taking place in the flask. The flask or other vessel in which the water is being boiled should have another outlet provided for the steam ; this may conveniently consist of a tube leading to the bottom of a beaker in which there are
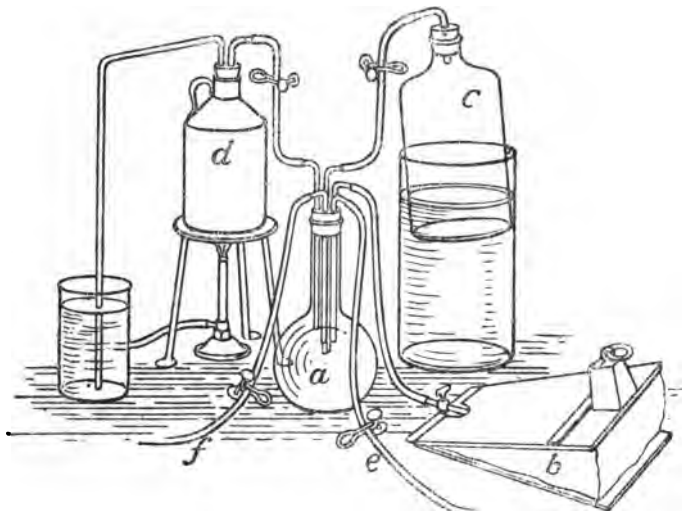
Fig. 53.—Experimental preparation of sulphuric acid.

about four or five inches of water. When the connection between the water-flask and the other is closed, the steam forces its way through the water in the beaker ; when this pipe is opened, the steam takes the channel offering least resistance, viz. into the flask. Fig. 53 shows the whole arrangement. *a* is the flask in which the reaction goes on ; *b* is a bladder containing sulphur dioxide under a weight ; *c* a gas-holder containing nitric oxide; *d* is the water-flask with escape tube leading into beaker ; *e* conveys air from gas-bag not shown in figure ; *f* is the exit tube for the waste gases. A description of the gas-holder is given in the laboratory hints for this chapter. The flask having been thoroughly dried, and everything being

in readiness, allow a slow current of air, sulphur dioxide, and nitric oxide to pass into the flask ; the ruddy fumes at first formed disappear, and a crystalline deposit is observed on the sides of the flask. Now shut off the whole of these and admit steam ; the crystalline compound disappears, nitrous fumes are evolved, and sulphuric acid condenses and collects at the bottom of the flask. Then re-admit sulphur dioxide, and in the presence of steam the nitrous fumes disappear ; add air— they are again formed; keep up a slow current of all the bodies— sulphuric acid collects at the bottom of the flask. Take out a few drops of the liquid ; test in the usual way with barium chloride and hydrochloric acid.

Place the remainder in an evaporating basin and apply heat. At first water is given off; finally dense suffocating fumes of sulphuric acid are evolved. Remove the flame immediately these are perceived ; a thick, oily-looking liquid remains.

In the manufacture of sulphuric acid, the sulphur dioxide may be produced by burning sulphur or by roasting sulphur ore (pyrites) in a suitable furnace. In this way a mixture of sulphur dioxide and air is formed. The reaction between the various bodies occurs in large chambers made of timber framing and lined with sheet lead, the joints being made air-tight by soldering the edges of the lead together by the oxyhydrogen blowpipe. Fig. 54 illustrates the general arrangement of a modern English sulphuric acid works. A A are two of a series of pyrites burners generating SO_2, which, passing along the flue B, heats the cast-iron troughs C, which are supplied with nitrate of soda and sulphuric acid through the funnels D, thus producing nitric acid fumes, which, together with the SO_2, pass onwards to the Glover tower E. This consists of a framework of stout timber, supporting a column of thick sheet lead, and lined with a wall of refractory bricks built without mortar, and diminishing in thickness towards the top. The remaining space is filled either with large flints or with reticulated or " pigeon-holed " brickwork, through the interspaces of which the gases pass upwards, meeting on their way sulphuric acid

trickling downwards from the tanks F, G, on the tower-top (of which more will be said presently), and so reach the first leaden chamber (No. 1), which consists of a timber framework lined with lead and supported on cast-iron pillars. Into this chamber steam from the steam-boilers is introduced by the jets j j set in the side of the chamber. Here the characteristic sulphuric acid reaction occurs, and the acid collects on the bottom of the chamber, which is formed as a huge saucer for this purpose. In this first chamber most of the SO_2 is converted into H_2SO_4, and the remaining gases, in which oxides of nitrogen begin to predominate, pass to a second similar chamber (No. 2), where they meet with more steam, and a further precipitation of sulphuric acid takes place, leaving the gases, still richer in nitrogen compounds and poorer in sulphurous acid, to pass into the next chamber (No. 3), where *nearly* the whole of the SO_2 is converted into liquid H_2SO_4. The remaining gases, which should now consist of residual nitrogen, a necessary excess of oxygen, oxides of nitrogen, and a trace of sulphurous acid, pass from this chamber by the flue H to the Gay Lussac or absorbing tower, which consists of a stout timber framework lined with lead, inside which is built a single brick wall without mortar.

The inside space in this tower is filled with large pieces of hard Durham coke, down which cold sulphuric acid, sp. gr. 1·75 (150° Twaddell), trickles from the cisterns I, J, in passing through the coke. This acid meets and absorbs the nitrogen oxides from the escaping gases, leaving only the excess of air, the atmospheric nitrogen corresponding to the oxygen taken up in the reactions, and a trace of SO_2. These pass from the tower by the exit flue X to the works chimney, which produces the draught for the apparatus, their escape being controlled by a damper, not shown in the figure. The number of chambers in a series varies from two to six in different works; their shape and size vary also within certain limits.

It remains to explain the working of the towers. Sulphuric acid of a sp. gr. 1·75 (150° Tw.) is run from the cistern marked "STRONG ACID" into a closed cast-iron vessel, K, technically called an "egg." When the egg is full, the valve communicating with the cistern is closed, and a valve opened which connects the egg with a powerful air-pumping engine, L, which, working up to a pressure of 60 lbs. per square inch, forces the acid out of the egg up the pipe M M into the cisterns I, J, on the top of the absorb-
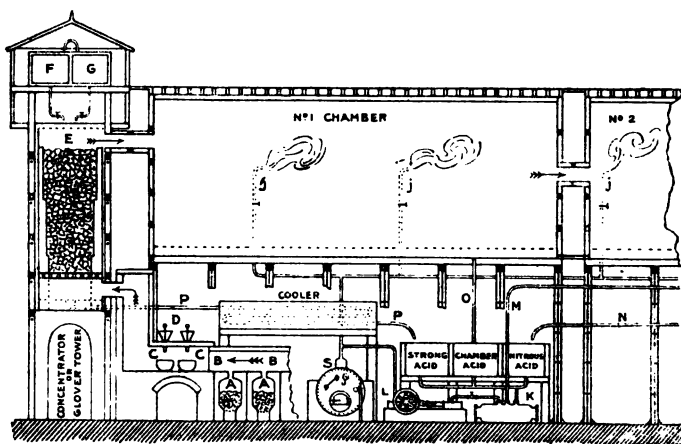
FIG. 54.—Manufacture

ing tower, whence it slowly trickles down through the coke, taking up the nitrous compounds, and running by the pipe N to the cistern marked "NITROUS ACID," whence, as required, it is run into the egg and "blown" through a pipe similar to M, but not shown in the figure, to the cistern F on the top of the Glover tower. The acid made in the chambers, having a specific gravity of 1·60 (120° Tw.), is drawn from time to time by the pipe O into the cistern marked "CHAMBER ACID," from which it is "blown" into the cistern G on the Glover tower. Now, by the taps shown in

the figure, the run of nitrous acid from F, and of chamber acid from G, is so adjusted that, after trickling down the hot flints or bricks, and meeting the hot burner gas on its way through the tower, the acid runs off by the pipe P, deprived of its nitrous compounds, which re-enter the chambers, and, concentrated by the heat to a sp. gr. of $1\cdot73$ to $1\cdot75$ ($146°$ to $150°$ Tw.), it then passes through a coil of lead piping immersed in cold water, thus cooling it to $60°$ Fahr., and
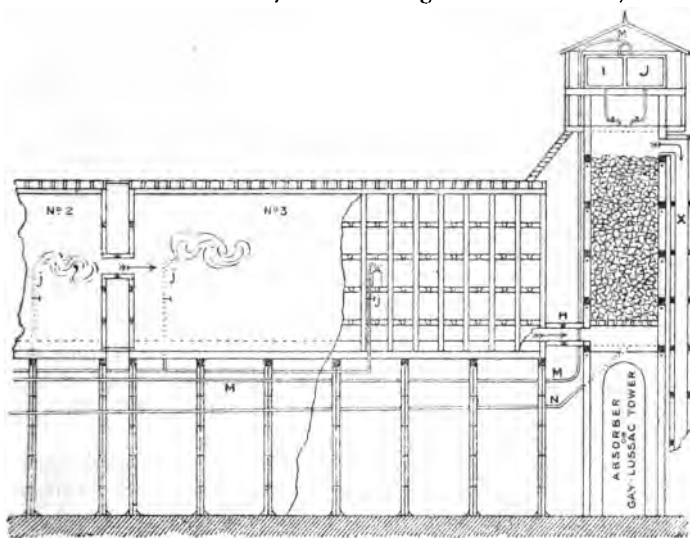
of sulphuric acid.

thence to the cistern marked "STRONG ACID," whence it is taken for use as required. The Glover and Gay Lussac towers therefore effect an economy by considerably reducing the amount of the most costly raw material used, *i.e.* nitrate of soda, and the Glover tower saves coals also by concentrating the acid, and thus also supplying steam to the chambers by utilizing the heat from the burners. Moreover, by cooling and therefore contracting the volume of the gases, it makes the existing chamber capacity more effective.

The acid is further concentrated by evaporation in vessels of either glass or platinum, until a density of 1·842 is reached.

The acid of strength 1·75 constitutes the "brown acid" of commerce; that of 1·842 density is known commercially as "oil of vitriol."

199. Properties.—Sulphuric acid in the pure state is a colourless, odourless liquid of oily consistency. It has a specific gravity of 1·842, and boils at about 338° C.; the high temperature of the boiling-point renders the acid specially suitable for the preparation of the more volatile acids, as nitric acid, from their salts; any excess of sulphuric acid and the resultant sulphate formed, being non-volatile at the temperature at which nitric acid boils, are thus easily separated.

Sulphuric acid has a very great attraction for water, with which it forms definite compounds; the union of the two is attended with evolution of great heat.

Experiment 192.—Place not more than a cubic centimetre of water in a test-tube, and add to it the same quantity of the concentrated acid; observe the heat developed, testing with a thermometer, if one be available.

Experiment 193.—Place a small quantity of sulphuric acid in an evaporating basin, and let it remain for a week; notice that at the end of that time the acid will have increased in volume from the absorption of moisture from the air.

From the avidity with which sulphuric acid absorbs water, it is largely used in the laboratory as a drying agent for gases. It also attacks most organic bodies, removing from them the elements of water; the preparation of carbon monoxide from oxalic or formic acid is an example of this action. When bodies have an excess of carbon, that element is deposited in the free state, as is the case with sugar.

Experiment 194.—Prepare a concentrated solution of sugar in water, and about one-eighth fill a beaker with it; add all at

once twice the volume of sulphuric acid ; the mixture suddenly froths up, with great heat ; a charred carbonaceous mass remains.

Experiment 195.—With dilute sulphuric acid make some marks on a piece of writing-paper, and dry it at a gentle heat ; as the water evaporates the acid carbonizes the paper.

Sulphuric acid, being a disbasic acid, forms two well-marked series of salts, the one of which is normal ; the other, still containing half the hydrogen, is acid.

At a white heat the acid is decomposed into water, sulphur dioxide, and oxygen.

200. Nordhausen Sulphuric Acid.—Nordhausen sulphuric acid may be looked on as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphur trioxide : it is named after a town in Saxony, where it is prepared in large quantities by first drying ferrous sulphate, and at a stronger heat decomposing it. Supposing the whole of the water were removed before the decomposition of the salt, the change might be thus represented :—

$$FeSO_4 \quad = \quad FeO \quad + \quad SO_3.$$
Ferrous sulphate.   Ferrous oxide.   Sulphur trioxide.

It is impossible, however, to first drive off the whole of the water, and a portion of the sulphur trioxide being hydrated, the remainder is dissolved—

$$2FeSO_4 + H_2O = 2FeO + H_2SO_4, SO_3, \text{ or } H_2S_2O_7.$$
Ferrous sulphate.   Water.   Ferrous oxide.   Nordhausen sulphuric acid.

The molecule of sulphur trioxide, in Nordhausen sulphuric acid, being only held in feeble combination, is readily driven off by heat.

Summary.

Sulphur trioxide is a non-acid body produced by the union of sulphur dioxide with oxygen ; the two combine when passed over red-hot spongy platinum. It has no action on litmus, but has a great affinity for water, with which it produces sulphuric acid.

x

Sulphuric acid is a compound of great importance : it is formed by the oxidation of sulphurous acid either by the atmosphere or oxidizing agents, as nitric acid, or hydroxyl.

Oxy-acids are considered by some chemists to contain hydroxyl. In oxidation by nitric acid the nitrogen peroxide formed oxidizes, a further quantity of sulphurous acid being reduced to nitric oxide, which is immediately reconverted into the higher oxide by the oxygen of the air. Sulphuric acid is manufactured by the reactions occurring between sulphur dioxide, oxygen, nitric acid, and steam. The dilute acid is concentrated by evaporation. Nordhausen sulphuric acid is prepared by heating ferrous sulphate. Sulphuric acid is a colourless, odourless liquid, having a great attraction for water. Being a dibasic acid, it forms two series of salts called sulphates.

OBJECT DEMONSTRATION.

Examine appearance of hermetically sealed sulphur trioxide ; also of brown sulphuric acid, oil of vitriol, and Nordhausen sulphuric acid.

LABORATORY DIRECTIONS.

The apparatus necessary for Exp. 191 should be obtained from the general apparatus in the laboratory. The cork fitted to the large flask should be soaked in melted paraffin. The instrument makers sell bladders, which may be used for the sulphur dioxide ; a bullock's bladder, however, answers equally well. To fit it up, soften the neck by soaking in water, pass a piece of glass tubing through, and bind round firmly with thin copper binding wire ; the bladder must be *dry* when used, as otherwise the sulphur dioxide is dissolved. Do not fill it long before required for use, and, when done with, squeeze out any gas which remains ; blow out the bladder with air, and again empty ; this will get rid of the sulphur dioxide. The bladder should be put away full of air. In arranging the bladder under a weighted board, take care that it is so fixed that there is no danger of the weight rolling on to the other parts of the apparatus. The air may be stored in a similar bladder, or, if there be an oxy-hydrogen limelight apparatus at hand, the *oxygen* bag may be used ; after the experiment *completely empty* the bag. The little gas-holder recommended for the nitric oxide is

a very useful piece of apparatus in the laboratory. To prepare one, take a deflagrating jar holding three pints or two quarts; fit to the top a paraffined cork, through which bore a hole and pass a bent piece of glass tube. Get a beaker or other vessel an inch or two higher than the jar, and of such a size that it easily slides up and down in it; fill this with water, and slip over the glass leading-tube a piece of indiarubber tubing and a screw tap. To fill the jar, attach the gas generating apparatus to the tube; the jar as it fills rises higher; when filled, shut off the screw tap. The weight of the jar is sufficient to force the gas out of the holder as required.

CHAPTER XXII.

BROMINE, IODINE, AND FLUORINE.

201. The Halogens.—The three elements, bromine, iodine, and fluorine, together with chlorine already described, constitute the group known as the "halogens." As most acids are oxy-acids, their corresponding salts must contain oxygen; but the halogens yield salts which are binary compounds by direct union with the metals. These salts, from their similarity to sea-salt, are termed "haloid" salts, and hence the name halogens given to the elements from which, by combination with the metals, they are produced.

The relations of the members of this group to each other are very interesting, but may be studied much better after some knowledge is gained of the elements themselves.

Bromine.—Symbol, Br. Atomic weight, 79·75. Density, 79·75. Specific gravity as gas, 5·51; as liquid, 3·18. Molecular weight, Br_2, 159·5. Molecular volume, ☐☐.

202. Occurrence.—Like chlorine, this element is never found free in nature, but in combination with other elements, usually either sodium, potassium, or magnesium. Balard, in 1826, discovered bromine in the mineral matter contained in sea-water; it also occurs in certain mineral deposits, particularly in the vast salt deposits of Stassfurt, in Germany.

203. Preparation.—The first step in the preparation of bromine is to separate the bromides from the chlorides with which they are associated. The solid salts are dissolved, and then concentrated by evaporation ; the chlorides, being less soluble, first crystallize out and leave a mother-liquor in which the bromides predominate. There are two reactions by which bromine may be obtained from this liquid. If chlorine be passed through the solution, bromine is liberated according to the following equation :—

$$\underset{\substack{\text{Potassium}\\\text{bromide.}}}{2\text{KBr}} \quad + \quad \underset{\text{Chlorine.}}{\text{Cl}_2} \quad = \quad \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2\text{KCl}} \quad + \quad \underset{\text{Bromine.}}{\text{Br}_2.}$$
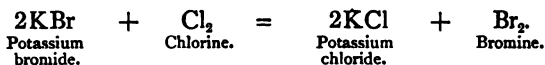
The bromine at first set free imparts a reddish-brown colour to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured off from the watery layer underneath. On this ethereal solution being treated with potassium hydrate, its red colour disappears, bromide and bromate of potassium being formed—

$$\underset{\text{Bromine.}}{3\text{Br}_2} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6\text{KHO}} = \underset{\substack{\text{Potassium}\\\text{bromide.}}}{5\text{KBr}} + \underset{\substack{\text{Potassium}\\\text{bromate.}}}{\text{KBrO}_3} + \underset{\text{Water.}}{3\text{H}_2\text{O}.}$$
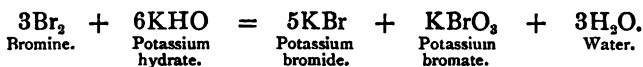
The ether may be distilled off and re-collected ; the solid residue of bromide and bromate is ignited in order to decompose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained ; the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid, when an analogous reaction occurs to that which takes place when a chloride is similarly heated—

$$\underset{\substack{\text{Potassium}\\\text{bromide.}}}{2\text{KBr}} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3\text{H}_2\text{SO}_4} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{\text{MnO}_2} =$$

$$\underset{\substack{\text{Hydrogen}\\\text{potassium sulphate.}}}{2\text{KHSO}_4} + \underset{\substack{\text{Manganese}\\\text{sulphate.}}}{\text{MnSO}_4} + \underset{\text{Bromine.}}{\text{Br}_2} + \underset{\text{Water.}}{2\text{H}_2\text{O}.}$$
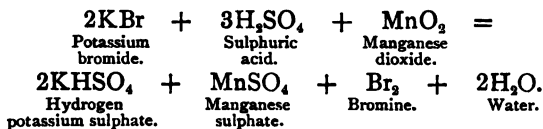
At times the mother-liquor, instead of being treated

with chlorine, is evaporated down to dryness, and the residue mixed direct with sulphuric acid and manganese dioxide; but in this case, as chlorides are always present in greater or less quantity, the bromine is liable to be contaminated with chlorine.

Experiment 196.—Take some potassium bromide, dissolve it in water, and pass chlorine gas through the solution; notice that the colour deepens through the liberation of the bromine. After some time, two-thirds fill a large test-tube with the solution, and thoroughly cool by holding under a stream of cold water. Next add some ether, close firmly with the thumb, and shake the tube; then hold the tube still for the ether to collect at the surface, keeping the top closed all the while with the thumb until the two liquids have completely separated from each other. Notice that the ether leaves the watery solution almost colourless. (If the solution of bromine in ether is too concentrated, it falls to the bottom; in this case add more ether, and again shake.) Pour off the ethereal solution; and, shaking up after each addition, add potassium hydrate solution until the colour disappears. Evaporate the solution to dryness, and ignite; potassium bromide remains.

Experiment 197.—Powder some potassium bromide, mix with manganese dioxide; place the mixture in a test-tube, and add concentrated sulphuric acid. Heat very gently; bromine vapour is given off in abundance, and collects in the upper part of the tube. Make this experiment in the stink closet.

204. Properties.—Bromine at ordinary temperatures is a dark red liquid, so heavy that glass floats readily in it. It gives off a deep reddish-brown vapour at ordinary temperatures, with a smell resembling that of chlorine, only far more intense. Bromine freezes at $-22°$ C. and boils at $63°$ C. Water dissolves bromine; the solution possesses bleaching powers, but not to such an extent as chlorine. In this, as in its other reactions, bromine and chlorine closely resemble each other; but bromine is the less active of the two, and is displaced from its compounds by chlorine.

Bromine combines with hydrogen to form a colourless fuming gas, hydrobromic acid, HBr, very similar to hydro-

chloric acid. The bromides in appearance and properties closely resemble the chlorides.

Bromine vapour is very similar to nitrogen peroxide in appearance: the following tests distinguish the one from the other. On shaking with a small quantity of ether, bromine is dissolved, and imparts its characteristic tint to the ether; nitrogen peroxide does not affect the colour. If to the bottle or jar containing bromine vapour a solution of potassium hydrate be added, the colour is removed. If this solution be very slightly acidulated by the addition of dilute nitric acid, and then silver nitrate added, there is a precipitate of silver bromide. Similar treatment causes no precipitate with nitrogen peroxide.

Bromides may be readily detected by the reaction with sulphuric acid and manganese dioxide, which liberate bromine in the free state.

Iodine.—Symbol I. Atomic weight, 126·53. Density, 126·53. Specific gravity as gas, 8·74; as solid, 4·95. Molecular weight, I_2, 253·06. Molecular volume, ⬚

205. Occurrence.—Iodine, as well as bromine and chlorine, is found in sea-water, but in much smaller quantities. There are certain varieties of seaweed which absorb the iodides and store them up in their tissues; from these the iodine of commerce is procured.

206. Preparation.—Such seaweeds as are sufficiently rich in iodides are dried and then burned; the ashes constitute the substance known as kelp. This kelp is next treated with sulphuric acid and manganese dioxide, when iodine is liberated, according to the equation—

$$2NaI + 3H_2SO_4 + MnO_2 =$$

Sodium iodide.   Sulphuric acid.   Manganese dioxide.

$$2NaHSO_4 + MnSO_4 + I_2 + 2H_2O.$$

Hydrogen sodium sulphate.   Manganese sulphate.   Iodine.   Water.
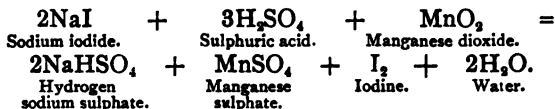
It should be observed that chlorine, bromine, and

iodine are liberated from the chlorides, bromides, and iodides by a precisely similar reaction.

Experiment 198.—Mix some powdered potassium iodide with manganese dioxide and concentrated sulphuric acid in a small retort. Heat gently; purple vapours arise and condense to a blue-black solid on the neck of the retort.

207. Properties.—Iodine is at ordinary temperatures a dark-coloured (blue-black) solid, which gives off small quantities of vapour of a splendid violet tint. At 115° C. iodine melts, and boils at a temperature of 200°. The violet tint of the vapour is then almost so dark as to appear black. The vapour possesses an odour resembling that of chlorine; this odour may be distinguished on smelling the substances at ordinary temperatures. Iodine is slightly soluble in water, to which it imparts a light sherry tint; it is much more soluble in solutions of potassium iodide, and also in alcohol and ether. All these solutions are brown in colour. Iodine also dissolves in carbon disulphide, to which it imparts a violet tint resembling that of its vapour.

In chemical reactions iodine closely resembles bromine and chlorine, but is less active than these elements; consequently iodine may be liberated from the iodides by the addition of either bromine or chlorine. On the other hand, the oxygen compounds of iodine are much more stable than those of bromine and chlorine.

Iodine is characterized by yielding a most remarkable reaction with starch. The addition of a minute trace of free iodine colours starch solution a deep blue. The colour vanishes on boiling, but reappears as the liquid cools. Iodine when in a state of combination does not give this reaction.

Experiment 199.—Prepare some starch solution by taking a small quantity of starch and shaking up with a test-tube full of cold water. Immerse this tube in a beaker of boiling water until the starch gelatinizes, stirring it meanwhile. As soon as

the thickening occurs, remove the tube and stand it in cold water until at the normal temperature.

To a small portion of the starch solution add a drop of solution of iodine in water; notice the blue coloration. Heat to boiling; note its disappearance and subsequent reappearance as the liquid cools.

To another portion of starch solution add some potassium iodide; there is no coloration. Add next a drop of aqueous solution of bromine; a blue colour at once forms as a result of the liberation of free iodine. Repeat the experiment, using chlorine water instead of bromine; the same effect is produced. Add the solutions of bromine and chlorine to separate portions of the starch solution; neither of these produces the blue coloration.

Iodine and hydrogen unite to form hydriodic acid, HI, which in general properties and behaviour resembles hydrochloric and hydrobromic acids. The iodides are very similar to the corresponding bromides and chlorides.

Fluorine.—Symbol, F. Atomic weight, 19·1.

208. Occurrence.—Fluorine occurs in nature in combination with calcium in fluor spar (calcium fluoride), CaF_2, and also in another mineral named cryolite. The teeth of animals also contain traces of fluorine.

209. Properties.—Fluorine is such an exceedingly active element that it is almost impossible to obtain it in the free state. Whenever liberated by any chemical reaction, it immediately attacks the vessel in which it is contained. Little, therefore, is known about this element.

210. Hydrofluoric Acid, HF.—This is the most important compound of fluorine, and, like hydrochloric acid, may be prepared by the action of sulphuric acid on one of its salts, as calcium fluoride. The acid is a gas soluble in water, and most corrosive in its action. The characteristic property of hydrofluoric acid is that it attacks and dissolves glass and other compounds of silica. If glass

be covered with a thin coating of wax, and then a design scratched on the surface with a needle, hydrofluoric acid dissolves the glass where the wax has been removed, and so produces a permanent etching of the design on the surface of the glass.

Experiment 200.—Warm a piece of glass and coat it with wax by letting a little melt on the surface and draining off the excess. When cool, write on this coating with the point of a needle. Mix in a small lead dish some powdered fluor spar and concentrated sulphuric acid ; warm *very gently;* pungent acid fumes are evolved. Lay the glass plate, with its etched face downwards, on the top of the dish, and let it remain for about five minutes. Remove the plate, and clean from the wax ; notice that the writing is permanently bitten into the glass.

In this reaction the calcium fluoride is decomposed according to the following equation :—

$$CaF_2 \;+\; H_2SO_4 \;=\; CaSO_4 \;+\; 2HF.$$
Calcium fluoride.   Sulphuric acid.   Calcium sulphate.   Hydrofluoric acid.
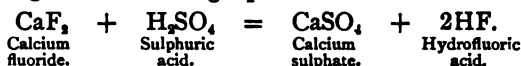
211. Review of the Halogens.—It will be seen that the members of this group of elements are characterized by possessing a remarkable similarity to each other. The connection between chlorine, bromine, and iodine is much closer than that with fluorine. Of these first three elements chlorine is a gas, bromine a liquid, and iodine a solid at ordinary temperatures. The density of the series increases with chlorine as the lowest and iodine as the highest. The chemical activity diminishes with the increase in density. Fluorine has a lower atomic weight than chlorine, and possesses greater chemical activity. The salts of these elements are very much alike; those of the same metal commonly crystallize in the same form.

Summary.

The group called halogens consists of chlorine, bromine, iodine, and fluorine.

Bromine is a dark red-coloured liquid evolving vapours of

the same colour, occurs in sea-water, and is obtained from the bromides by action of sulphuric acid and manganese peroxide. Bromine is similar in general behaviour to chlorine, but possesses less activity, and may be displaced from its compounds by chlorine.

Iodine is a dark grey solid which, when warmed, evolves deep violet-coloured vapours. Iodine is found in the ashes of seaweeds, and is obtained by treatment with sulphuric acid and manganese dioxide. Iodine also resembles chlorine in chemical behaviour, but is even less active than bromine. Iodides are decomposed by either free bromine or chlorine. Iodine is characterized by imparting a deep blue colour to starch solution ; it only possesses this property when in the free state.

Fluorine is so active that it is practically unknown in the free state : its principal compound is hydrofluoric acid, which possesses the property of dissolving glass.

OBJECT DEMONSTRATION.

Examine and compare specimens of chlorine, bromine, and iodine ; also of the chlorides, bromides, and iodides of potassium or sodium.

LABORATORY DIRECTIONS.

Remember that ether is very inflammable, and that it evolves vapour with great rapidity ; the vapour mixed with air is explosive ; in consequence great care must be exercised in bringing a light near ether. Small quantities only should be used at a time. A store-bottle should be kept, and a small one filled from it in a room where there are no lights burning.

As bromine vapour possesses such an overpowering smell, take care to get as little as possible of it about the room or laboratory.

In making a starch solution, take care not to have it too thick ; it should be sufficiently dilute to pour as readily as oil.

Hydrofluoric acid is very corrosive ; care must therefore be taken that none of it gets on the skin.

CHAPTER XXIII.

PHOSPHORUS AND SILICON.

Phosphorus. — Symbol, P. Atomic weight, 30·96. Density, 61·92. Specific gravity of ordinary variety, 1·83.

Molecular weight, 123·84. Molecular volume, ⊞ ·

Phosphorus is distinguished from all other elements we have so far described by there being four instead of two atoms in the molecule. The conventional symbol above given is intended to indicate, not that the molecule of phosphorus is twice the normal volume, but that, with the same molecular volume as other bodies in the gaseous state, it, the molecule, contains four atoms.

212. Occurrence.—Phosphorus is not found free in nature, but occurs in many igneous rocks; thus minute crystals of minerals containing phosphorus may be discerned by the microscope in granite. These rocks, by their decomposition, produce soil which also contains phosphorus as phosphates. These are assimilated by plants, and are found especially in the seeds; thus considerable quantities of phosphorus occur in wheat. In their turn animals assimilate the phosphates of vegetable food, and use them in building up certain compounds occurring in the brain and elsewhere, but more especially in the formation of bone, the mineral part of which, or bone-ash, consists largely of calcium phosphate. From this compound the phosphorus of commerce is prepared.

213. Preparation.—The first step in the preparation of phosphorus is to mix bone-ash with two-thirds of its weight of sulphuric acid diluted with water. Calcium phosphate is insoluble, but under this treatment is transformed into a soluble acid-phosphate, commonly known as super-phosphate of lime. The following equation represents the change which occurs :—

$$\underset{\substack{\text{Calcium} \\ \text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Sulphuric} \\ \text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Calcium} \\ \text{hydric phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium} \\ \text{sulphate.}}}{2CaSO_4.}$$
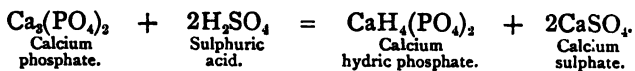
The calcium sulphate is allowed to settle, and then the clear solution of acid phosphate is evaporated down to the consistency of a syrup and mixed into a paste with powdered charcoal. This is dried, and then heated to low redness in an earthenware retort, the stem of which dips under water.

The first result of the application of heat is that the acid or hydric-phosphate loses its water, being converted into a salt known as the metaphosphate—

$$\underset{\substack{\text{Calcium} \\ \text{hydric phosphate.}}}{CaH_4(PO_4)_2} = \underset{\substack{\text{Calcium} \\ \text{metaphosphate.}}}{Ca(PO_3)_2} + \underset{\text{Water}}{2H_2O.}$$

The metaphosphate is, at the high temperature, decomposed by the charcoal; thus :—

$$\underset{\substack{\text{Calcium} \\ \text{metaphosphate.}}}{3Ca(PO_3)_2} + \underset{\text{Carbon.}}{10C} = \underset{\text{Phosphorus.}}{P_4} + \underset{\substack{\text{Calcium} \\ \text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Carbon} \\ \text{monoxide.}}}{10CO.}$$
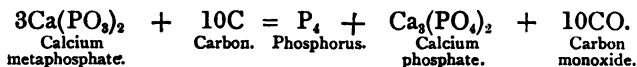
The phosphorus thus produced distils over, and is purified by redistillation and squeezing through washleather under warm water.

214. Properties.—Phosphorus is an almost colourless (slightly yellow) and transparent solid, having at ordinary temperature the consistency of bees'-wax, and may be cut with a knife. At the freezing-point it becomes considerably harder and more brittle; it then shows, on being broken, evidences of crystalline structure. Phosphorus melts at a temperature of $44\cdot3°$, and boils at $290°$ C.; the vapour is

colourless. When exposed to the air phosphorus is seen to evolve small quantities of smoke, and in the dark is distinctly luminous. From this property it has received its name, which signifies light-bearer. The fumes emitted consist of phosphorus trioxide, P_2O_3, and the light is due to slow combustion of the phosphorus. This element is characterized by its great inflammability; at a temperature of about 44°, a very little over its melting-point, it takes fire, and, as the student already knows, burns brightly with the formation of phosphorus pentoxide. Phosphorus is easily ignited by a slight amount of friction. Phosphorus is insoluble in water, slightly soluble in alcohol or ether, and readily soluble in carbon disulphide. Owing to the readiness with which it undergoes oxidation, phosphorus is kept under water, which liquid it does not decompose.

Experiment 201.—Cut some phosphorus, under water, into small fragments, and carefully wipe them thoroughly dry. Add carbon disulphide to them in a test-tube; notice that the phosphorus dissolves readily and completely. Pour a few drops of the liquid on a dry crumpled newspaper; the liquid rapidly evaporates and leaves a residue of finely divided phosphorus. This oxidizes so rapidly that it takes fire spontaneously, and also ignites the paper.

215. Red or Amorphous Phosphorus.—In addition to the yellow variety, phosphorus occurs in another totally distinct form, known as red or amorphous phosphorus. If ordinary phosphorus be maintained at a temperature of 240° for some time, it is more or less completely changed into an opaque reddish mass, without any alteration of weight. This, on purification from the ordinary form, constitutes amorphous phosphorus. This modification differs most remarkably from the yellow kind. It is not luminous when exposed to air; does not oxidize, and so need not be kept under water. It remains solid up to a temperature beyond 250°, and does not take fire when heated in the air until 260° is reached. At this point it

becomes changed into the yellow variety, and burns. If the heating be conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, proving most clearly that the two varieties are only allotropic modifications of one and the same element. Further, both, on being burned, produce the same weight of phosphorus pentoxide. Amorphous phosphorus is insoluble in carbon disulphide.

The change from the yellow to the red variety is much hastened by the presence of iodine in small quantities.

Experiment 202.—Place a piece of phosphorus, the size of a pea, in a long and narrow test-tube; drop on it a very small fragment of iodine: combination at once occurs, with the formation of a small quantity of phosphorus iodide. Heat gently; the phosphorus melts and takes fire, but soon exhausts the whole of the air in the tube. Continue to warm gently for a little time, and most of the phosphorus will be seen to become of a dark-red colour. Cork up the tube and allow it to cool. When quite cold, pour some carbon disulphide into another tube and put away the bottle, and then from the tube pour the disulphide on to the altered phosphorus. Cork up and allow the tube to stand for some time, giving it an occasional shake. Pour off the carbon disulphide, and a residue of amorphous phosphorus remains.

Take a little commercial red phosphorus and note the absence of odour, also its non-luminosity. Heat it on a sand-bath or in an iron spoon; note that it requires to be heated to a high temperature before it commences to burn.

Phosphoretted Hydrogen.—Formula, PH₃. Molecular weight, 33·96. Density, 16·98. Specific gravity, 1·17.

216. Preparation.—On boiling a strong solution of caustic soda or potash with phosphorus, a spontaneously inflammable gas is evolved, having the odour of putrid fish, and approximately the composition PH_3. This gas is phosphoretted hydrogen, or phosphine.

Experiment 203.—Fit to an 8-oz. flask a cork and rather large delivery tube, with its end leading into a pneumatic

trough containing water, and arrange in a retort stand. In the flask place a few fragments of caustic potash together with some small pieces of phosphorus and a little water. Pass coal gas into the upper part of the flask, so as to completely displace the whole of the air; then cork up tightly. Gently heat the flask; bubbles of gas arise and displace the coal gas. In a short time each bubble, as it rises to the surface of the water in the trough, bursts into flame and generates an extremely beautiful vortex ring of smoke.

At this stage collect over the trough a jar of the gas, and, having tightly corked it, expose for some days to the light. The inside of the jar will be found to be covered with a yellow film; and if it be opened the gas will be found to have lost its property of spontaneous inflammability. Apply a light; it burns with readiness.

The reaction by which phosphoretted hydrogen is thus produced is a somewhat complicated one, and may be thus expressed :—

$$P_4 + 3KHO + 3H_2O = 3KH_2PO_2 + PH_3.$$

Phosphorus. Potassium hydrate.   Water.   Potassium hypophosphite.   Phosphoretted hydrogen.
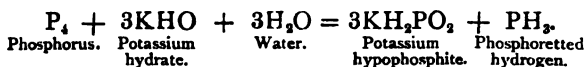
In addition to the phosphoretted hydrogen, PH_3, traces of another phosphide of hydrogen, P_2H_4, are formed. It is the presence of these which causes the gas to inflame spontaneously. The gas on standing loses this property, because the second phosphide, P_2H_4, suffers decomposition.

In the above method of preparing the gas, milk of lime (*i.e.* lime suspended in water) may be employed instead of caustic potash.

217. Properties.—Phosphoretted hydrogen is a colourless gas with an unpleasant odour of putrid fish. The gas is inflammable, and a non-supporter of combustion.

Phosphoric Acid. —Formula, H_3PO_4. **Molecular weight, 97·84.**

218. Preparation.—When phosphorus is burned in air or oxygen, phosphorus pentoxide is formed, according

to an equation already familiar to the student. If the pentoxide be dissolved in water, a hissing noise is produced, and phosphoric acid formed—

$$P_2O_5 \quad + \quad 3H_2O \quad = \quad 2H_3PO_4.$$
Phosphorus   Water.   Phosphoric acid.
pentoxide.

A method commonly employed for the preparation of this body is to oxidize phosphorus with nitric acid, when the following reaction occurs :—

$$P_4 \quad + \quad 10HNO_3 \quad + \quad H_2O \quad = \quad 4H_3PO_4 \quad + \quad 5N_2O_3.$$
Phosphorus.   Nitric acid.   Water.   Phosphoric acid.   Nitrogen
                                                                       trioxide.

The solution, on evaporation at the close of the reaction, yields a viscid liquid, from which colourless crystals of phosphoric acid may be obtained.

Experiment 204.—Thoroughly dry a large bell jar and plate on which it may stand. Wipe a piece of phosphorus quite dry, and also a deflagrating spoon. Burn the phosphorus in the bell jar, and allow the pentoxide to subside. Add a few drops of water, and notice the hissing noise as combination occurs.

One-third fill a beaker about 6 inches high with a mixture of two parts concentrated nitric acid and one of water. Cut a few fragments of phosphorus and drop them into the acid. Heat gently in a stink-cupboard; nitrous fumes are evolved, and the phosphorus is dissolved. If the action ceases before the whole of the phosphorus disappears, add a little more acid, and so dissolve the whole. At the close of the reaction evaporate down the liquid until it attains a temperature of 150° C. Phosphoric acid remains.

219. Properties.—There are not only several acids of phosphorus, but also several varieties of phosphoric acid, depending on the number of molecules of water with which a molecule of phosphoric anhydride is united. That described is the common or ortho-phosphoric acid. This acid contains three atoms of replaceable hydrogen, and so is tribasic. In the normal salts the whole three atoms are replaced by metals, but in the acid salts either one or two

Y

atoms of hydrogen may remain. The following series is illustrative of the various salts of phosphoric acid :—

H_3PO_4 Phosphoric acid.
NaH_2PO_4, Dihydric sodic phosphate.
Na_2HPO_4, Hydric disodic phosphate.
Na_3PO_4, Normal sodic phosphate.

Of these compounds the disodic phosphate is neutral to litmus, the monosodic salt has an acid, and the trisodic salt an alkaline reaction.

Silicon.—Symbol, Si. Atomic weight, 28·0. Specific gravity of crystals, 2·49.

220. Occurrence.—Next to oxygen this is the most plentiful of all the elements ; its oxide, SiO_2 occurs in the free state, as flint and quartz ; and also in combination as one of the principal constituents of most rock formations except those of coal and limestone. Silicon does not occur free in nature, and its properties as an element need not here be described.

Silicon Dioxide, Silica.—Formula, SiO_2. Molecular weight, 59·92. Specific gravity as quartz, 2·6.

221. Occurrence.—As has already been mentioned, this compound is widely distributed in nature as a rock constituent. Quartz and amethyst are examples of a crystalline variety, and agate, chalcedony, opal, and flint consist of silica in an amorphous form mixed with more or less of the crystalline variety.

222. Properties.—Quartz is, when pure, transparent and colourless : it is so hard that it scratches glass. Quartz crystals consist of hexagonal prisms capped with hexagonal pyramids. Quartz is insoluble in water and all acids, except hydrofluoric acid, by which it is readily attacked. It is not liquefied by the heat of the strongest furnaces, but may be melted into a glassy mass by the oxy-hydrogen blowpipe.

Silica is sometimes termed silicic anhydride, because with water it forms acids and unites with bases to produce salts. Prolonged boiling with concentrated solutions of caustic potash or soda dissolves crystalline silica very slowly, but has a more rapid action on the amorphous varieties. When fused with either of the alkaline carbonates an alkaline silicate is formed—

$$SiO_2 \quad + \quad 2K_2CO_3 \quad = \quad K_4SiO_4 \quad + \quad 2CO_2.$$

Silica.   Potassium   Potassium   Carbon dioxide.,
           carbonate.   silicate.
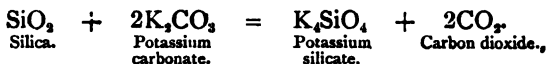
Carbon dioxide escapes, and the remaining silicate is soluble in water, and constitutes the substance known as water-glass. If hydrochloric acid be added to the solution, potassium chloride and silicic acid are formed—

$$K_4SiO_4 \quad + \quad 4HCl \quad = \quad 4KCl \quad + \quad H_4SiO_4.$$

Potassium   Hydrochloric   Potassium   Silicic
silicate.   acid.   chloride.   acid.
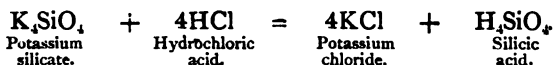
If the solution be concentrated the silicic acid separates out as a gelatinous mass, but if sufficiently dilute it remains dissolved. On the solution being placed in a drum with the bottom made of parchment paper, and this floated in its turn in a vessel of water, the potassium chloride, being a crystalline body, diffuses through the membrane, and a pure solution of silicic acid remains behind. In this way a solution of quartz or silica is produced. This solution may be concentrated by careful evaporation until it contains about 14 per cent. of silica ; but the solution of this degree of strength is liable to assume the gelatinous form. On further concentration the silica separates out, and on evaporation to complete dryness remains as an amorphous white powder, insoluble in water and acids.

Experiment 205.—Reduce some flint or quartz to an impalpable powder : this is most easily effected by heating to redness and plunging into cold water. The fragments then powder somewhat easily. Fuse some potassium carbonate in a platinum crucible over a good foot blowpipe flame. When quite tranquil at a bright red heat, add a small pinch of the powdered silica;

notice that effervescence occurs, and that the silica is entirely dissolved. Continue the addition of silica so long as it is dissolved. Allow the crucible to cool, and dissolve out its contents with water. Add dilute hydrochloric acid until the solution has an acid reaction, then evaporate to complete dryness; ignite gently, and treat with water. Potassium chloride dissolves, and insoluble silica remains.

The formula of silicic acid has been written H_4SiO_4, but there are several other modifications of the acid produced by the combination of water and silicic anhydride in various proportions. The silicates are extremely complex in composition, frequently containing several metals and many molecules of silica, derived not merely from one, but frequently two or more modifications of silicic acid.

Summary.

Phosphorus occurs as a constituent of igneous rocks; obtained from phosphates by reduction with carbon; is inflammable; exists in two forms, which differ widely from each other in properties.

Phosphoretted hydrogen is prepared by heating phosphorus with caustic potash solution, and is an inflammable gas, with odour of putrid fish. The presence of liquid phosphoretted hydrogen causes the gaseous variety to become spontaneously inflammable.

Phosphoric acid is formed by hydration of phosphoric anhydride or by oxidation of phosphorus by nitric acid. This acid is tribasic, and forms an extended series of salts.

Silicon is a widely distributed element, but does not occur free in nature; its most important compound is silica.

Silica is the only known oxide of silicon, and occurs as quartz, flint, and in other rocks. Is insoluble in acids except hydrofluoric; dissolves when fused with alkaline carbonates to form soluble silicates, hence is viewed as the anhydride of silicic acid. From a solution of alkaline silicates, by the addition of hydrochloric acid, soluble silicic acid is formed, and may be obtained in the pure state by diffusion of the alkaline chlorides through a membrane. Silicic acid solution, on being evaporated to dryness, yields silica once more in the insoluble form.

OBJECT DEMONSTRATION.

Examine native calcium phosphate, bone-ash, and commercial calcium superphosphate.

Examine and compare yellow and red phosphorus.

Note flint, quartz, opal, and other native varieties of silica.

Examine gelatinous silica and water-glass.

LABORATORY DIRECTIONS.

The student will already be sufficiently familiar with the properties of phosphorus to know that it requires extremely careful handling. In those experiments where carbon disulphide is used, be careful that the main supply bottle is kept at a distance from the phosphorus.

At times, in Exp. 202, the phosphorus re-ignites on the top of the tube on the removal of the cork; should it do this, cork again and keep for a day or two. Of, if wished, a current of carbon dioxide may be passed down the tube until the whole of the phosphorus vapour is displaced. The carbon disulphide may then be poured in in safety.

In the preparation of phosphoretted hydrogen, the coal gas is passed in in order to expel any acid, as otherwise the phosphoretted hydrogen would take fire within the flask and possibly burst it. Remember that if any air remains with the coal gas the phosphoretted hydrogen may explode the mixture, and so cause considerable damage by scattering the molten phosphorus. In the case of an inexperienced student, it would be safer to displace the air by carbon dioxide rather than by coal gas.

At the close of the experiment, allow the liquid in the flask to cool until water is drawn up into it from the trough. Pull out the cork, holding it in a duster; the gas within the flask will take fire; therefore have in readiness a jug of cold water, with which at once fill the flask to the brim.

Platinum crucibles and dishes must be handled carefully. When heated over the blowpipe flame, they should be supported in a pipeclay triangle.

IDENTIFICATION OF GASES AND OTHER BODIES.

In the great majority of our preceding experiments the line of study has been that of verifying the statements contained in the text. For example, the student is told that, on the application of heat to mercury oxide, oxygen is evolved and mercury remains. He next proceeds to determine the truth of this by himself heating mercury oxide, and testing for the evolved oxygen, and noting the presence of the residual metallic mercury.

As an introduction to the principles of analysis, and an exercise in both the mental and experimental operations of research, the following course of work is recommended. The essential difference from the preceding experiments is that a part only of the facts are known, and the student is required to ascertain the remainder for himself. For example, an unknown body is given to him, and he is required to apply a certain test, such as heating the substance, when he must note the result and draw what conclusions he is able. It is recommended that, in going through the following course of work, the teacher, or some other person, should set the student the various exercises irregularly, so that the latter may not know on what he is working until he has determined the same by making the directed experiments.

ACTION OF HEAT ON BODIES.

First note the appearance of the following substances ; then apply heat, and observe what takes place. If possible, identify the body and its products, if any. Introduce the substance itself direct in the flame, or, if a powder, heat it in a dry, clean test-tube.

1. Piece of light white wire—burns with very white light, leaving white ash. Probably **Mg**.

2. Piece of heavy bright white wire—unchanged by heat. Probably **Pt**.

3. Reddish-yellow powder—glows and leaves a bluish-black residue. Probably **mixture of Cu and S**.

4. Brick-red powder—turns black, greyish sublimate; insert glowing splinter in tube — relights. Resulting bodies : mercury and oxygen ; body is **HgO**.

5. White tabular crystals, non-deliquescent — decrepitates, melts, evolves gas ; smell same — odourless ; apply lighted splinter—burns very brightly. **O from KClO₃**.

6. Black powder—does not melt; test whether it gives off gas by introducing glowing splinter — burns very brightly. Probably **O from KClO₃ and MnO₂**.

7. Colourless, odourless liquid—boils ; insert lighted splinter in vapour—goes out ; liquid boils all away without residue ; insert strips of litmus paper in a portion—neutral. Liquid is **H₂O**.

8. Black powder—does not melt ; introduce glowing splinter —no gas evolved ; heat a little on Pt. foil—glows and burns away. Substance is **charcoal**.

9. White powder—volatilizes entirely without melting, and recondenses in cooler part of tube. Probably **AmCl**.

10. White, needle-shaped crystals, non-deliquescent—melts, gives off gas, which relights glowing splinter ; gas reddish in tint, and characteristic nitrous odour. O and nitrous fumes from probably **KNO₃**.

11. White, needle-shaped crystals, slightly deliquescent— melts, evolves gas which relights glowing splinter ; pour a little NaHO solution over a fresh portion, and heat gently—smell of NH₃. Substance is **NH₄NO₃**, and gas evolved is **N₂O**.

12. Yellow powder — melts to clear yellow liquid, which becomes thick and darkens in colour ; finally boils and deposits yellow crystalline sublimate in cooler parts of the tube. **S**.

13. Bluish-black substance — melts, evolves violet-coloured fumes, which recondense in cooler parts of tube. **I**.

ACTION OF WATER ON SUBSTANCES.

Note appearance ; then add water in the cold—note effect ; boil—observe what occurs ; allow to cool, and observe result.

1. Greyish-white fragments—cold water absorbed ; substance becomes very hot, and breaks up into white powder or paste. Probably **CaO**.

2. White powder—with cold water effervesces violently ; close the mouth of the tube loosely with the thumb till action is .

over; then pour the gas, but not the liquid, into another tube containing lime-water ; shake up the second tube—its contents become milky. CO_2, from probably mixture of Na_2CO_3 and tartaric acid.

3. White substance—with cold water dissolves; hot water more dissolves ; solution cools, part separates out—formation of crystals.

ACTION OF HYDROCHLORIC ACID ON BODIES.

1. Bluish-white metal—gas evolved in cold, which takes fire on application of light, and burns with scarcely luminous flame. Probably H evolved by action of Zn.

2. Heavy black powder—gas evolved, deep yellow colour, pungent, suffocating odour. Cl evolved by action of MnO_2.

3. White powder—brisk effervescence in cold, gas evolved, neither inflammable nor supporter of combustion ; gas poured into tube containing lime-water—turns latter milky. CO_2 from carbonate.

ACTION OF DILUTE SULPHURIC ACID ON BODIES.

1. Bluish-white metal—inflammable, odourless gas evolved. Probably H evolved by action of Zn.

2. Brownish-black powder—colourless, inflammable gas evolved, with odour of rotten eggs. SH_2 from sulphides.

ACTION OF CONCENTRATED SULPHURIC ACID ON BODIES.

1. White powder — colourless gas evolved in the cold, yielding pungent acid fumes in contact with air, non-inflammable, non-supporter of combustion. HCl from chlorides.

2. White crystals — no action in cold ; colourless, inflammable gas evolved on heating ; on pouring gas into second tube containing lime-water, turns it milky. CO and CO_2 from $H_2C_2O_4$.

3. Inflammable liquid with characteristic spirituous smell—with five parts acid to one of liquid, colourless gas evolved, inflammable, and burns with bright smoky flame. C_2H_4 from C_2H_5HO.

4. White acicular crystals—nitrous odour ; liquid condenses in upper part of tube. Repeat experiment, using small retort and test-tube as receiver—colourless or faintly yellow liquid collects, intensely acid to litmus paper, and with characteristic odour. HNO_3 from nitrate.

5. Fragments of red metal—gas evolved, with characteristic odour of burning sulphur, non-inflammable and non-supporter of combustion. SO_2 evolved by action of Cu.

ACTION OF NITRIC ACID.

Fragments of red metal—colourless gas evolved, which turns red immediately on coming in contact with air. **NO** evolved by action of **Cu**.

SCHEME FOR IDENTIFICATION OF GASES.

In the preceding chapters the student will have become acquainted with the following, among other gases : O, H, Cl, HCl, CO, CO_2, N, NH_3, N_2O, NO, SH_2, and SO_2. Given any one of these gases, he should be able, by systematic testing, to identify the same.

The gas for examination might conveniently be supplied to the student in any one of the three following forms of containing vessel : (1) a bag of rubber or other suitable material ; (2) pumped in under pressure in a small metal gas-cylinder ; (3) in a glass gas-holder, such as is described for storage of hydrogen over water on p. 129.

NOTE.—This last arrangement would exclude HCl, NH_3, and SO_2, which are too soluble in water even to permit their temporary storage in this manner.

Table for Systematic Examination of Gases.

Cautiously allow a little of the gas to escape from the containing vessel, and smell same.					
Gas possesses marked odour.	Gas either odourless, or odour not very marked. O, H, CO, CO_2, N, N_2O.				
Characteristic irritating odour —Cl.	Fill a jar with the gas in the pneumatic trough over water, and apply a lighted taper.				
Pungent odour, acid fumes— HCl. **Characteristic ammoniacal odour—NH_3.** **Nitrous odour, ruddy fumes —NO.**	The gas supports combustion—O or N_2O. Partly fill another jar with the gas, and add one or two bubbles of NO from a second jar.		The gas is inflammable —H or CO. Light a jar of the gas, and when nearly burnt out, close with a cover. Add lime-water, and shake up.		The gas is non-inflammable and a non-supporter of combustion —CO_2 or N. Fill a jar with the gas, add lime-water, and shake up.
Odour of rotten eggs—SH_2. **Odour of burning sulphur —SO_2.**	Ruddy fumes produced. The gas is **O.**	No reaction. The gas is **N_2O.**	No reaction. The gas is **H.**	Lime-water turns milky. The gas is **CO.**	Lime-water turns milky. The gas is **CO_2.**	No reaction. The gas is **N.**

CONFIRMATORY TESTS.

Cl.—Fill a jar with the gas over water; notice that the colour is yellow. Introduce a lighted taper ; the taper burns with a very sooty flame and formation of acid fumes.

HCl.—Fill a dry jar by downward displacement, and introduce lighted taper ; it is extinguished, and gas does not burn. Add a little water, and shake up ; gas dissolves, and solution is acid to litmus paper.

NH₃.—Fill a dry jar by upward displacement, and introduce a lighted taper ; taper is extinguished, and the gas at the mouth of the jar momentarily takes fire. Add a little water to a jar of the gas, and shake up ; gas dissolves, and solution is alkaline to litmus paper.

NO.—Fill a jar with the gas over water ; it is colourless ; on removal of cover it becomes ruddy. Introduce a lighted taper ; it is extinguished, and the gas does not burn.

SH₂.—Fill a jar with the gas over water, apply a lighted taper ; the gas burns with a yellow deposit of sulphur. Shake up another jar of the gas with a little water, and add a few drops of a solution of lead nitrate ; black ppt. of PbS.

SO₂.—Fill a dry jar by downward displacement, and introduce a lighted taper ; it is extinguished, and the gas does not burn. Shake up the gas with a little water ; solution first reddens and then bleaches blue litmus paper. Add two or three drops of strong nitric acid to the solution, and boil in a test-tube, then add $BaCl_2$ solution ; ppt. of $BaSO_4$ from H_2SO_3, oxidized to H_2SO_4.

O.—Three-parts fill a jar with the gas over clean water, put on cover, and shake vigorously so as to wash the gas—hold under the surface of the water, and remove the cover ; the water does not rise, showing the gas is practically insoluble. Draw a little of the gas from this jar into the mouth through a glass tube ; it is tasteless. Plunge *very feebly* burning sulphur into the gas ; it burns brilliantly.

N₂O.—Partly fill a jar with the gas, and treat as directed for oxygen ; after shaking, the water rises in the jar, showing the gas to be soluble. Draw a little into the mouth ; it has a characteristic sweetish taste. Plunge very feebly burning sulphur into the gas ; it is extinguished.

H.—Fill two jars with the gas, turn one upside down, and

simultaneously remove the covers from both ; at the end of twenty seconds apply a light to each. From the one upside down very little gas has escaped, and that remaining burns ; the hydrogen has altogether escaped from the other, showing that the gas is extremely light.

00.—Treat exactly as directed for hydrogen ; the contents of each of the two jars burn equally well, showing that the gas has practically the same density as air.

00_2.—Partly fill a jar with the gas, and shake up with water —open under water ; the water rises, showing the gas to be somewhat soluble. Pour the gas from a jar *downwards* over a lighted candle ; it flows down and extinguishes the candle, thus showing its high density. Draw a little into the mouth ; it has a characteristic taste. Smell a jar of the gas ; it has a characteristic odour. (NOTE.—In strictness, CO_2 should be placed among the odorous gases, but the odour is not sufficiently intense to warrant it always being thus recognized. Should it be so identified, the confirmatory tests, including that of lime-water, should be tried with it.)

N.—Treat as directed for CO_2 ; the gas is practically insoluble ; being of less density than air, does not pour *down* on lighted candle ; has neither taste nor smell.

PRINCIPLES OF ANALYSIS.

THE student is now in a position to proceed further in his study of practical chemistry by learning the principles of analysis and their application to the separation and recognition of unknown bodies.

There are two descriptions of analysis—qualitative, by which the constituents of a substance are detected, and quantitative, by which their actual amount is determined. The first only of these will be dealt with in this work, the study of quantitative analysis belonging to a more advanced stage of chemistry.

The substances that a student is likely to require to analyze are either metals (including alloys) or salts. In some few cases he may meet with free acids.

The following pages provide, first of all, for an introductory and very elementary course of analysis, in which the student is only expected to recognize and detect, in powders soluble in water or dilute acid, in each case not more than two bases and one acid selected from the undermentioned :—

Lead, copper, iron, zinc, calcium, potassium, and the compound radical ammonium.

Carbonic, nitric, sulphuric, and hydrochloric acids.

An account of the analytical reactions of these metals and acids follows ; and also systematic tables for the analysis of unknown substances which may contain them.

There is next given a more extended scheme, which contains in addition an account of the analytical reactions of the metals and inorganic acids undermentioned, and also systematic tables for the analysis of unknown substances which may contain all or any of them :—**Silver, mercury, bismuth, cadmium, tin, arsenic, antimony, chromium, aluminium, manganese, nickel, cobalt, barium, strontium, magnesium, and sodium; sulphuretted hydrogen, hydrobromic, hydriodic, hydrofluoric, chloric, boric, phosphoric, and silicic acids.** The reactions of the following organic acids are also given, and tables are appended for the analysis of their salts with inorganic bases :—**Hydrocyanic, formic, acetic, benzoic, succinic, oxalic, tartaric,** and **citric acids.**

There are two distinct methods of making the qualitative analysis of a body. The first is called the "**dry way**," because experiments are made on the substance without its being dissolved. These experiments consist of heating it on charcoal, and in other ways observing its behaviour under certain conditions. In the second method the body is first obtained in solution, and then subjected to the reaction of different reagents. The production of a precipitate having a characteristic colour or other distinctive properties enables the analyst to recognize the substance, and also to separate it by filtration from those still remaining in solution. Each of these courses has its advantages, and usually a combination of the two is preferable to one only taken singly. In the tables given further on there are first directions for a preliminary examination by the dry way, and afterwards a wet analysis. The results of the one should confirm those of the other, and often the metals difficultly recognized by the one method give very characteristic reactions by the other.

The term **reaction** is applied to any chemical change employed in analysis. The substance applied to produce the change is called a **reagent.**

OPERATIONS.

Many analytic experiments require the use of methods that so far are unknown to the student. Of these the most important is the use of the blowpipe for heating purposes. There are several forms of this instrument, two of which are shown in Fig. 55, *b* and *c*: but for laboratory use the conical form devised

by Black is the most convenient ; it is represented in Fig. 55, *a*. The conical tube is preferably of brass, and has a bone or ivory mouthpiece at the smaller end ; the other is closed, and near it through the side of the tube a smaller one projects, to the end of which the jet is attached.   The moisture of the mouth
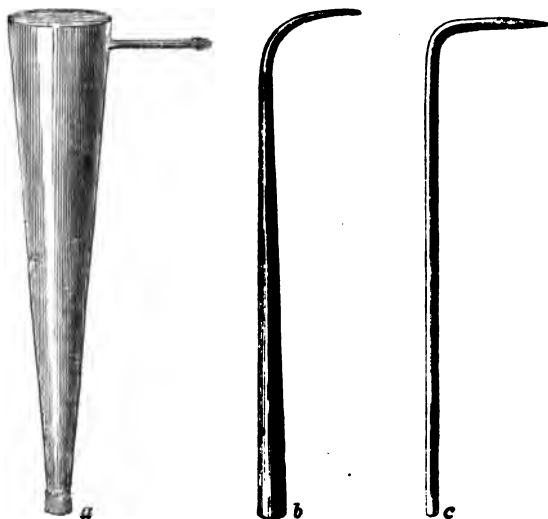
FIG. 55.—Various forms of blowpipe.

collects, while blowing, in the end of the cone instead of being blown out through the jet.   In using a blowpipe, the air must be forced out by the cheeks, and *not* from the lungs.   A practical lesson from a teacher will do more toward teaching how this is done properly than a long description can do.   Still, by attention to the following directions, the art may in most cases be readily attained.   First, with the mouth closed, inflate the cheeks with air from the lungs as full as possible ; then keep on breathing through the nose with the cheeks still distended.   Before long it will be found that breathing can proceed in this way, whether the cheeks be full or empty.   In the next place, prepare a small glass jet by drawing out a piece of fine quill tubing in the flame.   While trying the experiment of breathing with the

cheeks distended, introduce the end of this jet between the lips: the elasticity of the cheeks will slowly force the air out of the mouth through the jet, but this will not interfere with the act of breathing. When the mouth is nearly empty, refill it by forcing some of the air contained in the throat and lungs into it. This is the most difficult part of the whole process, but a very little practice should enable the operator to do this without ceasing to blow.

A blowpipe may be used with either a spirit or oil lamp, but in all cases where gas is obtainable it will be found most convenient. A suitable form of flame is obtained by the use of a jet to be dropped inside the tube of a Bunsen burner, or a tube with the same shaped orifice is sometimes made to screw on to the base of the Bunsen (as in Fig. 56) instead of the ordinary brass tube, which is first unscrewed. With a tube of this kind, the ring must be turned so as to shut off the air at the bottom of the burner.

Fig. 56.—Bunsen arranged for use with blowpipe.

There are two varieties of blowpipe flame, known respectively as the "reducing" and "oxidising," from their action on oxides and metals. The reducing flame is shown in Fig. 56. To produce it, hold the jet of the blowpipe just outside the flame, and blow gently ; the flame should appear of a luminous yellow tinge, through its still containing unoxidized carbon. This exerts a powerful reducing action, the carbon combining

Fig. 57.—Oxidizing flame with blowpipe.

with the oxygen of many oxides when placed in it. An "oxidizing" flame (Fig. 57) is produced by placing the blowpipe

jet within the flame, and blowing rather harder. The flame should be sharply defined. The point of the fine blue cone in the middle of the flame is the region of the greatest heat. Slightly beyond this there is an excess of air, and this readily yields oxygen to any substance capable of combining with it.

Substances may be held in the blowpipe flame on a piece of *good* charcoal. This is a difficult article to obtain. Prepared charcoal blocks answer very well; those known as "Bunring's patent" are very good. A small cavity to receive the body should be cut out with a penknife. When one experiment has been made, the face of the charcoal must be cut away until a clean surface is exposed. Other supports are sometimes used for particular experiments, as platinum wire, a thread of asbestos, or the fragment of carbon produced by charring a lucifer match.

Several metallic oxides dissolve in fused borax, and produce a glass of characteristic colour. These reactions are performed most easily by obtaining a bead of borax on a loop of fine platinum wire. Fig. 58 shows a single and double loop of the actual size they should be made. To form a bead,
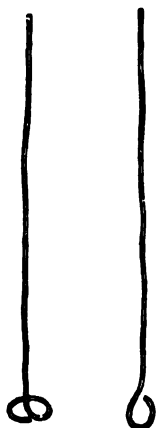
FIG. 58.—Platinum wire looped for borax bead.

make the wire red-hot in the Bunsen flame, and then dip it into some powdered borax. Next heat it either in the Bunsen or blowpipe flame until the borax melts down into a colourless and transparent bead. A fragment of the substance to be tested is then to be placed on the bead, which is again fused. The characteristic colour makes its appearance as the bead cools.

For washing precipitates, and to hold distilled water for general purposes, a "wash-bottle" is required. To make this, get a 24-oz. flask, and fit a good cork to the mouth. Through this bore two holes; bend two pieces of glass tubing to the shape shown in 1, Fig. 59, the acute-angled one reaching to the bottom of the flask, and the other just through the cork. From another piece of tubing about 4 inches long make two jets, as shown in 2, Fig. 59, by drawing out the tube slowly after softening it in the middle over the Bunsen flame. The ends of all the

tubes must be rounded with the blowpipe, and the jet attached to the wash-bottle by a small piece of indiarubber tubing. On blowing into the shorter tube a fine stream of water issues from the jet, and may be sent in any direction by bending the tube at the indiarubber joint. To obtain a larger stream, invert the bottle, and the water will run from the shorter tube.

While working at analysis, the student should bear in mind the following few directions. Test-tubes, beakers, and all other apparatus used for analysis must be **scrupulously clean**. Never put anything away dirty; a piece of apparatus that would take a minute to wash immediately after use will probably require five after lying by for a week. Give glass apparatus in general a couple of washings with tap water and then one with distilled water; allow them to drain; it is not necessary to wipe the insides of such vessels dry. Whenever water is required for purposes of solution, distilled water must be used.
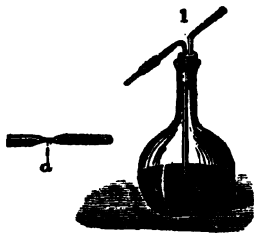
FIG. 59.—Wash-bottle and jet.

REACTIONS OF THE METALS.

Each of these reactions must be carefully performed by the student : he should endeavour to remember the appearance of the precipitate or other change produced, so that if he tries the same experiment on an unknown body and gets the same result, he will be able to recognize it and thus identify the substances present.

For each metal a salt is named that may be conveniently used for its reactions; they would, however, be the same with most other salts. In a laboratory, solutions are usually kept ready made up for the use of students.

LEAD.—Lead nitrate may be used.

Dry. Heated on charcoal with blowpipe in the reducing flame, a soft metallic bead of lead is produced, which marks paper; yellow incrustation.

A fragment the size of a shot is quite sufficient for this experiment : the salt should be first powdered for *all* blowpipe experiments.

z

Incrustations usually consist of oxide, formed by the combustion of the metallic vapour as it passes out of the reducing flame, and deposited on the cooler surrounding charcoal. Incrustations must not be confounded with the ash of the charcoal itself.

Wet. HCl—white ppt. of $PbCl_2$ somewhat sol. in cold H_2O, much more sol. in hot H_2O, from which it re-crystallizes on cooling : insol. in AmHO, being converted into PbHOCl.

From the solubility of $PbCl_2$, this metal cannot be entirely removed from a solution by HCl: when the solution is very dilute, no ppt. is obtained.

In making the wet tests, place about half an inch of the test solution in a small test-tube, and add the reagent, as HCl, drop by drop ; observe carefully the changes produced as each drop falls into the liquid. When various solvents are to be tried on the same ppt., it must be washed between the application of each. Heavy ppts. may easily be washed by decantation : drain off as much of the liquid as possible, and then fill up with water ; shake up the tube, allow the ppt. to subside, and again decant ; repeat the operation a second time, and then the ppt. will be sufficiently washed. When the ppt. does not so readily subside, it must be washed by filtration. The contents of the tube are to be poured on a filter and the liquid allowed to drain through ; then fill up the filter from the wash-bottle, directing the stream at each portion of the ppt., let the washing water drain *completely* away, and then refill ; when the second lot of washings have passed through, the ppt. may be transferred again to a test-tube by pushing a hole through the bottom of the paper and washing it through, or the funnel may be held inverted and the ppt. washed out with a vertical stream of water from the wash-bottle. The ppt. may sometimes be taken out of the paper with the point of a penknife or a small spatula.

In every case use as small quantities of each substance as possible : large ppts. take more time to wash, and render every operation of analysis tediously long.

H_2S—black ppt. of PbS insol. in dilute HCl, oxidized in part to $PbSO_4$ by HNO_3, insol. in NaHO.

K_2CrO_4—lemon-yellow ppt. of $PbCrO_4$.

COPPER.—Copper sulphate may be used.

Dry. Heated on charcoal with Na_2CO_3 and KCN in reducing flame—small malleable red beads of Cu.

The Na_2CO_3 and KCN should be in equal quantities: about five times as much of the mixture as of the copper compound should be

taken : the whole quantity should not be more than would fill a cavity the size of half a pea.   Careful and continuous blowing is requisite.

Heated in borax bead—in oxidizing flame the bead is green while hot, blue when cold ; in reducing flame, the bead is red when cold.

The red bead in R.F. is difficult to get.   If the smallest scrap of metallic Sn is placed on the bead and fused with it, the reduction takes place immediately.

Heated on platinum wire in Bunsen flame—imparts to it an intense green colour.

Wet. H_2S—black ppt. of CuS insol. in dilute HCl, slightly sol. in SAm_2, insol. in NaHO.

AmHO—greenish-blue ppt. sol. in very slight excess to a deep blue solution.

KCy—yellowish-green ppt. of $CuCy_2$ sol. in excess ; H_2S produces no ppt. in this solution.

K_4FeCy_6—brown ppt. of Cu_2FeCy_6.

IRON, FERROUS COMPOUNDS.—Ferrous sulphate may be used.

Dry.   Heated on charcoal in reducing flame—brownish residue remains, which is attracted by a magnet.

In borax bead—in O.F. yellowish-red bead, in R.F. green bead.

Wet.   AmHO—white ppt. of $Fe(HO)_2$, rapidly changing in colour to green, and finally being changed into reddish brown $Fe_2(HO)_6$.

It is very difficult to procure a ferrous salt absolutely free from ferric salts, but by dissolving the crystals of $FeSO_4$ in cold H_2O they may be obtained almost free from any ferric impurity.   The reduction of a trace of ferric salt may be produced by adding to the solution a drop of H_2SO_4 and a fragment of granulated Zn.   The small quantity of Zn that may be dissolved does not interfere with the reactions.

Am_2S—black ppt. of FeS, sol. in dilute HCl.

Potassium ferrocyanide (K_4FeCy_6)—white ppt. of Fe_2FeCy_6, rapidly changing to dark blue.

Potassium ferricyanide ($K_6Fe_2Cy_{12}$)—dark blue ppt.

FERRIC COMPOUNDS.—Ferric chloride (Fe_2Cl_6) may be used.

Dry.   Same as those of ferrous compounds.

Wet. AmHO—reddish brown ppt. of $Fe_2(HO)_6$.

Am_2S—reduces ferric to ferrous salts and ppts. FeS with the separation of S. HCl dissolves the FeS with evolution of H_2S, when the S may be observed as a white cloud in the solution.

K_4FeCy_6—dark blue ppt. (Prussian blue).

$K_6Fe_2Cy_{12}$—no ppt., reddish-brown coloration.

AmCyS—blood-red coloration.

ZINC.—Zinc sulphate may be used.

Dry. Heated on charcoal in reducing flame—incrustation, yellow while hot, white when cold.

Strongly ignited on charcoal or Pt loop, allowed to cool, treated with $Co(NO_3)_2$, and again ignited—the residue assumes a green colour.

Wet. Am_2S—white ppt. of ZnS, sol. in dilute HCl, insol. in acetic acid, and also in NaHO.

NaHO—white ppt. of $Zn(HO)_2$, sol. in excess, from which solution $Zn(HO)_2$ is not re-pptd. by AmCl.

CALCIUM.—Calcium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a yellowish-red flame coloration.

Wet. Am_2CO_3, with AmHO—white ppt. of $CaCO_3$ sol. in HCl or acetic acid.

H_2SO_4—from concentrated solutions ppts. $CaSO_4$; this salt is sol. in boiling Am_2SO_4.

Ammonium oxalate, $Am_2C_2O_4$—white ppt. from even very dilute solutions, sol. in HCl, but insol. in acetic or oxalic acids.

This test gives a ppt. with water from wells in chalk or limestone districts.

POTASSIUM.—Potassium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a violet coloration, which, when looked at through deep blue glass, appears of a reddish-violet colour.

Wet. $PtCl_4$ in presence of HCl—a yellow crystalline ppt. of $(KCl)_2PtCl_4$ insol. in dilute acids. The precipitation is hastened by the addition of a little of a mixture of alcohol and ether.

This reaction is best performed on a watch-glass placed on a piece

of white paper or porcelain ; a drop only of each reagent should be taken.

AMMONIUM.—Ammonium chloride may be used.

Dry. Heated in tube Am salts volatilize entirely, except the acid be fixed ; in which case NH_3 is liberated, and may be recognized by its smell.

Some Am salts are decomposed by heat, as $AmNO_3$; others, as AmCl, are again deposited as a sublimate.

For tube reactions small test-tubes may be used : where the heat required is intense, tubes may be employed made from "combustion" tubing (a difficultly fusible variety). Cut the tube, which should be ½-inch bore, into lengths of about 7 inches ; draw each of these pieces in the foot blowpipe flame off into two tubes ; seal up the bottom of each, and blow a small bulb. As in tube reactions it is wished to study sublimates, it is necessary that the sides of the tube should be kept clean. With this end in view, the salt should be introduced by means of a little gutter of paper. Take a piece of paper about 4 inches long and ⅜ inch wide ; fold this lengthwise in the middle, put the substance on this paper and carefully push it down the tube ; then hold the tube upright, give it one or two taps, and the substance will fall to the bottom of the tube ; withdraw the paper, and the sides of the tube will be found to be quite clean.

In heating these tubes, if any moisture condenses in the part near the mouth, they should be held so that it shall run *from* the hot part, and not toward it.

Wet. Heated with NaHO—ammoniacal odour.

$PtCl_4$ in presence of HCl—yellow crystalline ppt. of $(AmCl)_2PtCl_4$.

It is therefore necessary to remove Am salts by ignition previous to testing for K by $PtCl_4$.

REACTIONS OF THE ACIDS.

CARBONIC ACID, H_2CO_3.—Sodium carbonate may be used.

Dry. All carbonates, except those of K and Na, are decomposed by heat into oxides, with the evolution of CO_2. $BaCO_3$ and $SrCO_3$ require a white heat.

Wet. Dilute HCl added to the powdered salt—colourless odourless gas evolved, with effervescence, that turns lime-water milky.

In this and similar tests the salt itself is to be used, and not a

solution. Small quantities of CO_2 may be detected in the following manner :—Pour some $Ca(HO)_2$ in a test-tube ; put the salt in another; add HCl, and close the mouth of the tube with the thumb ; allow gas to escape slowly. Then, when the action is over, pour the gas into the $Ca(HO)_2$ test-tube, taking care to stop before any of the liquid follows (Fig. 60). Shake up the tube containing the CO_2 and $(CaHO)_2$: the latter is turned milky.

When small quantities have to be tested, the apparatus shown in

FIG. 60.—Pouring carbon dioxide
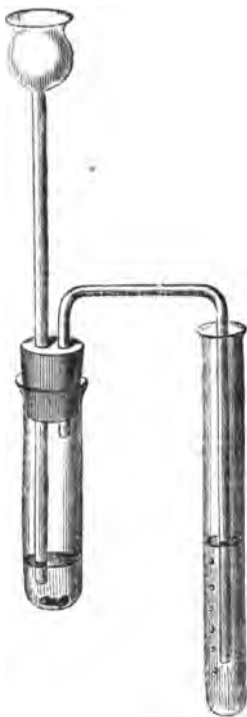
FIG. 61.—Testing for carbon dioxide.

FIG 62.—Nitric acid reaction.

Fig. 61 is often useful. The larger tube is fitted up with a thistle funnel and delivery tube. The whole of the gas generated may be driven into the smaller tube by blowing with an aspirator or hand-bellows (not the mouth) through the thistle funnel. Where special

accuracy is necessary, the air should be first freed from CO_2 by being passed through a solution of KHO.

Another method that is serviceable for the detection of traces of CO_2 is to place a glass rod dipped in $Ca(HO)_2$ in the mouth of the tube ; a film of $CaCO_3$ will be formed on it. Care must be taken, however, that the whole of the vapour of HCl has subsided, as its presence in quantity would prevent the formation of a ppt.

NITRIC ACID, HNO_3.—Potassium nitrate may be used.

Dry. Heated in tube—all nitrates are decomposed, one of the lower oxides of nitrogen and O being evolved. N_2O_3 and NO_2 may be recognized by their smell.

Heated on charcoal—nitrates deflagrate.

Wet. Heated gently with conc. H_2SO_4,—nitrates evolve HNO_3, which has a characteristic odour. On the addition of Cu turnings nitrous fumes are evolved.

$FeSO_4$ poured down the side of a test-tube containing a cold solution of a nitrate with an equal volume of conc. H_2SO_4,—dark brown ring where liquids meet (Fig. 62).

To the solution of the nitrate an equal volume of the H_2SO_4 should be added, and then the tube cooled by being kept for a minute or two in cold water ; the solution of $FeSO_4$ must be added carefully, so that the one liquid may float on the top of the other without immediately mixing.

HYDROCHLORIC ACID, HCl.—Sodiumchloride may be used.

Wet. Heated gently with conc. H_2SO_4—pungent fumes of HCl are evolved. The following chlorides are not readily decomposed by conc. H_2SO_4 :—Hg_2Cl_2, $HgCl_2$, AgCl, $PbCl_2$, $SnCl_2$, and $SnCl_4$.

Heated with conc. H_2SO_4 and MnO_2—all chlorides evolve Cl.

$AgNO_3$—white ppt. of AgCl, readily soluble in AmHO.

SULPHURIC ACID, H_2SO_4.—Potassium sulphate may be used.

Dry. Heated on charcoal with Na_2CO_3 in reducing flame— a sulphide is formed, recognized by the odour of H_2S on addition of HCl.

If the residue be placed on a silver coin, and then treated with HCl, a black stain of Ag_2S is produced.

Wet. $BaCl_2$—white ppt. of $BaSO_4$ insol. in acids.

DIRECTIONS FOR THE ANALYSIS OF UNKNOWN INORGANIC SUBSTANCES.

Observe the appearance of the substance. Note particularly whether it be metallic, as if so, no acids need be searched for. Powder the substance finely, and keep in a clean watch-glass, or if deliquescent, in a corked test-tube.

Should the substance be a liquid, test whether acid or alkaline to litmus paper. Evaporate a portion to dryness, and use the residue for the dry examination. If the solution is neutral to litmus paper, leaves no residue on evaporation, and is odourless and tasteless, it consists of pure water only. (Ether, alcohol, etc., would also leave no residue, but would be at once distinguished by their smell.)

Perform the experiments in the order in which they are given, as in the later ones it is presumed that the information from the earlier ones is in the possession of the student. Want of attention to this rule is a fruitful source of error with young students.

An account must be kept of each experiment as performed; a specimen of the results of analysis of a body as they should be written out is given on p. 349.

TABLES FOR THE EXAMINATION OF SUBSTANCES CONTAINING ONLY THE FOREGOING BASES AND ACIDS.

PRELIMINARY EXAMINATION BY THE DRY WAY.

I. HEAT A LITTLE OF THE POWDERED SUBSTANCE IN A TEST-TUBE OR PIECE OF SMALL COMBUSTION TUBING CLOSED AT ONE END AND A SMALL BULB BLOWN.

RESULT.	DEDUCTION. Presence of—
HN_3 is evolved . . .	**Am** salts.
Nitrous fumes evolved . .	**Nitrates.**
A white sublimate is formed [1]	**Am** salts.
	Confirm Am by treating a little of the original substance with solution of NaHO—NH_3 evolved.
	Am is present.

II. HEAT SOME OF THE SUBSTANCE ON CHARCOAL WITH THE BLOWPIPE IN OXIDIZING FLAME.

RESULT.	DEDUCTION. Presence of—
The substance deflagrates	**Nitrates.**
An infusible residue remains; white	**ZnO, CaO.**
	Moisten the white residue, when cold, with $Co(NO_3)_2$, and ignite strongly— green mass, **ZnO.**
Residue coloured . . .	**CuO, Fe₂O₃.**
	Heat a portion of the substance in borax bead.
	O.F. green while hot, blue when cold—**Cu.**
	O.F. pale yellow, R.F. olive-green bead—**Fe.**

[1] If there be no sublimate or other principal reaction, the confirmatory tests, etc., under the heading of "Deduction" are to be omitted,

III. HEAT THE SUBSTANCE WITH FUSION MIXTURE IN THE REDUCING FLAME.

RESULT.	DEDUCTION. Presence of—
An incrustation is formed without metallic bead ; yellow when hot, white when cold .	Zn.
A metallic bead is formed .	Pb, Cu.
Soft bluish-white malleable bead which marks paper ; yellow incrustation . .	Pb.
Small red malleable beads with black coating of oxide	Cu.

IV. DIP A CLEAN Pt WIRE, MOISTENED WITH HCl, INTO SOME OF THE SUBSTANCE, AND HEAT IN THE BUNSEN FLAME.

RESULT.	DEDUCTION. Presence of—
Bluish green flame coloration	Cu.
Yellowish red „ „	Ca.
Violet „ . „	K.

This preliminary examination must on no account be omitted. Many reactions other than those mentioned in the table will occur, but those only are introduced which are characteristic of the different elements and compounds. When the substance under examination is a mixture of several salts, the reactions of the one may hide those of the others. The student, therefore, must not in every instance assume that an element is absent because he does not get its particular reaction.

EXAMINATION IN THE WET WAY.

If the substance be solid, proceed to make a solution, remembering that the substance must first be finely powdered.

Test first its solubility in water by heating a small portion with H_2O in a test-tube ; if it be soluble, pass on to analysis. If not soluble in water, pass on to dissolving same in dilute acid, using, in the absence of Pb, hydrochloric acid, but in its presence, nitric acid. (The " Dry " examination will have revealed the presence or absence of Pb.)

Having ascertained the solvent required, make a fair amount of solution and call it "original solution" of the substance. Proceed to examine same by following table :—

To a portion of the original solution add HCl until it no longer produces a precipitate.				
White ppt. of **PbCl₂**. Filter and wash thoroughly with *cold* H₂O.	To the filtrate add sulphuretted hydrogen solution until it smells strongly of the gas. Heat gently.			
	Black ppt. of **CuS**. Filter and wash.	Boil the filtrate till free from SH₂, and add AmCl and AmHO in slight excess.		
		Green ppt. of **Fe(HO)₂**, or reddish brown ppt. of **Fe₂(HO)₆**. Filter and wash.	To the filtrate add SAm₂ in slight excess. Heat gently.	
			White ppt of **ZnS**. Filter and wash.	To the filtrate add AmHO and Am₂CO₃. Heat gently and allow to stand a few minutes.
				White ppt. of **CaCO₃**. Filter and wash. Evaporate the filtrate completely to dryness, and ignite so as to entirely drive off all ammoniacal salts. Dissolve residue in very little water, add HCl, PtCl₄, and a few drops of alcohol.
				Yellow crystal'ine ppt. of **(KCl)₂PtCl₄**.

When one of these reagents produces no ppt., pass on immediately to the addition of the next.

NOTE.—PbCl₂ is somewhat soluble in water, and therefore Pb, if present, will give a slight black ppt. of PbS on addition of H₂S. The confirmatory tests will distinguish between this and CuS.

Confirmatory Tests for above.

PbCl₂.—Heat the ppt. with water ; it dissolves and recrystallizes out on cooling. To portion of original solution add K₂CrO₄—yellow ppt. of PbCrO₄. Confirmed by dry reaction. **Pb is present.**

CuS.—Dissolve ppt. by boiling with conc. HNO₃; dilute, and add AmHO in excess—light blue ppt. of Cu(HO)₂, dissolving to deep blue solution. Confirmed by dry reaction. **Cu is present.**

Fe(HO)$_2$, or Fe$_2$(HO)$_6$.—Dissolve the ppt. in dilute HCl, add 1 drop conc. HNO$_3$, and boil add K$_4$FeCy$_6$—dark blue ppt. **Fe is present.**

ZnS.—Dry the ppt. and ignite on charcoal; then heat with Co(NO$_3$)$_2$—green mass. **Zn is present.**

CaCO$_3$.—Dissolve the ppt. in very dilute HCl, largely dilute with water, and add Am$_2$C$_2$O$_4$—white ppt. of CaC$_2$O$_4$. **Ca is present.**

(KCl)$_2$PtCl$_4$.—Take a little of the ppt. on Pt wire and heat in Bunsen flame—violet coloration. Test original substance for K by adding HCl (filtering off PbCl$_2$ if necessary), and adding PtCl$_4$ and alcohol —yellow crystalline ppt. of (KCl$_2$)PtCl$_4$. **K is present.**

Am Salts.—Test specially for these by heating the original substance with NaHO. Ammoniacal odour. **Am is present.**

EXAMINATION FOR ACIDS.

I. TREAT A LITTLE OF THE POWDERED SUBSTANCE IN A TEST-TUBE WITH DILUTE HCl ; WARM GENTLY.[1]

RESULT.	DEDUCTION. Presence of—
Colourless, odourless gas evolved, which turns lime-water milky . . .	**CO$_2$ from carbonates.**

II. TREAT ANOTHER PORTION OF THE POWDERED SUBSTANCE WITH CONCENTRATED H$_2$SO$_4$; WARM GENTLY.

RESULT.	DEDUCTION. Presence of—
CO$_2$ as on treatment with HCl. Nitrous fumes evolved and odour of HNO$_3$ . .	**HNO$_3$,** also indicated by deflagration on charcoal.
Pungent acid fumes evolved.	**HCl.**
	Add a little MnO$_2$—Cl is evolved from **chlorides.**

[1] When told to warm gently, the heat must not be sufficiently intense to drive off fumes of the acid reagent being used.

Confirmatory Tests for Acids.

CO$_2$.—The turning of lime-water milky is such a perfectly characteristic test for CO$_2$ that no further test is necessary.

HNO$_3$.—Confirm by adding FeSO$_4$ to aqueous solution of the substance mixed with H$_2$SO$_4$—brown ring coloration. **HNO$_3$ is present.**

HCl.—Treat a little of the original substance with water and a little dilute HNO$_3$; heat very gently, and to the solution add AgNO$_3$—white curdy ppt. of AgCl. **HCl is present.**

H$_2$SO$_4$.—This acid gives no reaction with either of the tests given. Treat a little of the original substance with H$_2$O and a little dilute HCl ; heat very gently, and filter from any insoluble residue if necessary. Test the filtrate or solution by adding ·BaCl$_2$—white ppt. of BaSO$_4$. **H$_2$SO$_4$ is present.**

Having thus made a complete analysis of the substance, the various bases and acids found should be entered at the foot of the account of the analysis in the student's note-book. Appended are the results of an analysis as they should be written. Remember that each experiment should be entered as performed.

Example showing how Analytic Results should be written.

Substance given for analysis—a bluish-white powder.

Heated a little of the substance in a dry tube.

Result.	*Deduction.*
No special reaction . . .	*Absence of Am salts and nitrates.*

Heated a portion on charcoal in oxidizing flame.

Coloured residue . . .	*CuO, Fe$_2$O$_3$.*
	Heated a portion in borax bead, O.F.—green while hot, blue when cold. Cu.

Heated with fusion mixture in reducing flame.

Bluish-green and violet flame coloration	*Cu and K.*

Dissolved substance easily in water.

To portion added HCl.				
No. ppt.	To same portion added SH₂ until smelling strongly; heated gently.			
	Black ppt. Filtered and washed.	Boiled off SH₂ from filtrate; added AmCl and AmHO.		
		No ppt.	To same portion added SAm₂.	
			No ppt.	To same portion added AmHO and Am₂CO₃; heated and allowed to stand.
				No ppt. — Evaporated filtrate to dryness; ignited, dissolved residue, and added HCl, PtCl₄, and alcohol.
				Yellow crystalline ppt.

Confirmatory Tests.

CuS.—*Dissolved black ppt. in conc.* HNO_3, *diluted and added AmHO, light blue ppt., dissolving to deep blue solution* Cu.

(KCl)₂PtCl₄.—*Heated ppt. in Bunsen—violet flame coloration. Confirmed* PtCl₄ *reaction by testing original substance—yellow crystalline ppt.* K.

Treated substance with dilute HCl.

No reaction .   .   .   . | CO_2 absent.

Heated substance with conc. H_2SO_4.

No reaction .   .   .   . | HNO_3 and HCl absent.

To portion of original solution added HCl and $BaCl_2$—*white ppt. of* $BaSO_4$—H_2SO_4.

Found: Metals—CuO, K₂O.
Acid—H_2SO_4.

FURTHER REACTION OF METALS.

For purposes of analysis the metals are arranged in five groups, depending on the insolubility of certain of their salts. This arrangement is shown in the following table, and the description of reactions follows the same order.

Group I.	Group II.	Group III.	Group IV.	Group V.
Metals whose chlorides are insoluble.[1] They may be precipitated by **Hydrochloric Acid.**	Metals whose sulphides are insoluble in dilute hydrochloric acid.[2] They may be precipitated by **sulphuretted Hydrogen**	Group III. A.[3]—Metals whose hydrates are insoluble in excess of ammonia and ammonium chloride. They may be precipitated by **Ammonium** in the presence of **Ammonium Chloride.**	Metals whose carbonates are insoluble in an alkaline solution. They may be precipitated by **Ammonium Carbonate** in the presence of **Ammonium Chloride and Ammonia.**	Metals not precipitated by any group reagent.
Silver as AgCl. Lead as PbCl$_2$. Mercury as Hg$_2$Cl$_2$.	Mercury as HgS.[4] Lead as PbS.[4] Bismuth as Bi$_2$S$_3$. Copper as CuS. Cadmium as CdS. Tin as SnS or SnS$_2$. Antimony as Sb$_2$S$_3$. Arsenic as As$_2$S$_3$.	Iron as Fe$_2$(HO)$_6$. Aluminium as Al$_2$(HO)$_6$. Chromium as Cr$_2$(HO)$_6$.	Barium as BaCO$_3$. Strontium as SrCO$_3$. Calcium as CaCO$_3$.	Magnesium. Potassium. Sodium. Ammonium.[5]
		Group III. B.—Metals whose sulphides are insoluble in an alkaline solution. They may be precipitated by **Ammonium Sulphide** in the presence of **Ammonium Chloride and Ammonia.**		
		Zinc as ZnS. Manganese as MnS. Nickel as NiS. Cobalt as CoS.		

[1] When solubility is referred to, water is always understood as the solvent, unless some other is stated.

[2] In each group the metals of those preceding are supposed to be absent, thus the metals of Group I. also form insoluble sulphides in HCl, but in analysis would be removed previous to the precipitation of Group II.

[3] Mercury and a few other metals form two series of salts in which the metal has different active atomicities.

[4] PbCl$_2$ is somewhat soluble in cold water, and thus a small quantity of lead is always found in Group II.

[5] The metals of Group III., A and B, are usually classed together as one group : for this reason the subdivision here adopted is referred to by letters instead of calling Group III. B, Group IV., as so doing would interfere with the usual numbers given to the groups.

[6] Ammonium is usually spoken of as a metal in analytic tables for the sake of brevity.

SILVER.—Silver nitrate may be used for both the dry and wet reactions.

Dry. Heated on charcoal with blowpipe in the reducing flame, a white malleable bead of silver is produced without incrustation.

Wet. HCl (or any soluble chloride) gives a white curdy precipitate of AgCl, which is turned violet by the action of light; the ppt. is insol. in hot H_2O, is sol. in AmHO, and re-pptd. by HNO_3.

H_2S—black ppt. of Ag_2S.

K_2CrO_4—dark red ppt. of Ag_2CrO_4.

The contents of tubes containing silver salts must not be thrown away, but should be placed in a bottle kept for the purpose.

MERCURY, MERCUROUS SALTS.—Mercurous nitrate may be used.

Dry. Heated in tube—a sublimate of globules of metallic Hg is produced.

The nitrate is first decomposed with the liberation of nitrous fumes and production of the oxide ; and this undergoes further decomposition into Hg and O. Other salts, as Hg_2Cl_2, sublime without decomposition.

Mixed with Na_2CO_3 or fusion mixture and heated in tube, all mercurous salts yield a sublimate of Hg globules.

The Na_2CO_3 or fusion mixture used must be perfectly dry. It is a good plan to fuse some in a platinum capsule and then powder it : keep in a well-stoppered bottle.

Wet. HCl—white ppt. of Hg_2Cl_2, blackened by the addition of AmHO.

H_2S—black ppt. of Hg_2S.

NaHO—black ppt. of Hg_2O.

$SnCl_2$—grey ppt. of metallic Hg.

MERCURIC SALTS.—Mercuric chloride may be used.

Dry. Same as for mercurous compounds.

Wet. H_2S—black ppt. of HgS insol. in HCl or HNO_3, sol. in aqua regia, insol. in NaHO.

The first trace of H_2S produces a white ppt., which changes through yellow to black. To all the sulphides of Group II. add a few drops of HCl and observe their insolubility.

NaHO—yellow ppt. of HgO.

SnCl₂—white ppt. of Hg₂Cl₂, changing with excess of SnCl to grey ppt. of Hg.

BISMUTH.—Bismuth nitrate may be used.

Dry. Heated on charcoal with Na_2CO_3—brittle yellowish white metallic bead ; surrounded by incrustation, dark orange while hot, lemon-yellow when cold.

Wet. H_2S—black ppt. of Bi_2S_3 insol. in dilute HCl, and in NaHO or SAm₂.

Much water added to solution—white ppt. of an oxy-salt.

This reaction takes place most readily with the chloride, $BiCl_3$; a ppt. of BiOCl is formed. From this property a salt of Bi may be dissolved in a small quantity of HCl and re-pptd., on dilution with H_2O. When this occurs in making solution of an unknown salt, the presence of Bi (or Sb, which acts similarly) may be suspected.

AmHo—white ppt. of Bi(HO)₃ insol. in excess.

CADMIUM.—Cadmium sulphate may be used.

Dry. Heated in tube—some salts, in particular CdBr, sublime, although difficultly.

This should be remembered, as Cd is thus sometimes mistaken for the other volatile metals.

Heated on charcoal with Na_2CO_3 in reducing flame—the metal is reduced, but is immediately oxidized and forms a brown incrustation.

Wet. H_2S—yellow ppt. of CdS, sol. in HCl unless very dilute ; sol. also in dilute H_2SO_4 ; insol. in NaHO.

The solubility of CdS in HCl, when not sufficiently dilute, leads frequently to its being undetected in Group II.

KCy—white ppt. of CdCy₂ sol. in excess, from which H_2S ppts. CdS.

TIN, STANNOUS SALTS.—Stannous chloride may be used.

Dry. Heated on charcoal with Na_2CO_3 and KCy in reducing flame—a white malleable bead, which is oxidized by HNO_3 to a white compound, $Sn_5O_5(HO)_{10}$.

Traces of a tin-salt heated in R.F. in a borax bead, coloured blue by Cu—change the colour to red.

Wet. H_2S—brown ppt. of SnS, insol. in dilute HCl, sol. in NaHO, or yellow SAm₂, re-pptd. by HCl.

$HgCl_2$—white ppt. of Hg_2Cl_2; if the stannous salt be in excess, a grey ppt. of Hg is formed.

Zn granulated—spongy ppt. of metallic Sn from acid solution.

$SnCl_2$ is readily changed into $SnCl_4$ and Sn_2Cl_2O by action of O. To hinder this, granulated Sn is usually placed in a solution of $SnCl_2$.

STANNIC SALTS.

Dry. Same as for stannous compounds.

Wet. A solution of stannic chloride may be used.

H_2S—yellow ppt. of SnS_2 insol. in dilute HCl, sol. in NaHO or SAm_2 re-pptd. by HCl.

Zn—same reaction as with stannous salts.

ARSENIC, ARSENIOUS COMPOUNDS.—Arsenic trioxide may be used; for the wet tests a solution in HCl.

Dry. Heated in tube—all salts sublime.

Heated in tube open at both ends—an odour of garlic may be observed.

To make this test, take a piece of combustion tube about 4 in. long, place the substance in the middle, and apply heat; the tube must be held slightly inclined; the odour is given off at the upper end.

Heated in a small tube with Na_2CO_3 and charcoal powder (black flux)—the compound is reduced and a grey, mirror-like sublimate of metallic As is formed. Heated on charcoal very gently with the reducing flame—garlic odour is observed, and a white incrustation some distance from the assay is deposited.

The substance heated in this way on charcoal is often called technically " the assay."

Wet. H_2S—yellow ppt. insol. in HCl. sol. in NaHO, and also in $AmHCO_3$.

Strips of clean Cu in solution acidulated with HCl, on gently heating—a greyish film of As_2Cu_5 is deposited, even from very dilute solutions. (Reinsch's test.)

On introducing a solution of any As compound into an apparatus in which H is being evolved, AsH_3 is formed, and may be recognized by special tests. Fit up a 4-oz. flask as a generating flask for the preparation of H from Zn and H_2SO_4 (Fig. 63), attach a $CaCl_2$ tube for drying, and to that a piece of ¼-inch combustion tubing, which has been narrowed in two or three places, as at *b*. Place in the flask some granulated Zn free from As and some water, add a very little strong pure

H_2SO_4; when the H has expelled the whole of the air from the flask, heat the tube at *b*, and continue the evolution of the gas for at least five minutes; if at the end of that time there is no sign of a mirror of As beyond the heated point, it may be assumed that the reagents contain no As. Light the flame as it issues from the end of the tube, and it will be seen to burn with the usual almost colourless flame of H. Add now through the funnel a few drops of the As solution; the colour of the flame changes to a livid blue, and it is seen to give off white fumes. Depress momentarily into the flame a porcelain crucible cover — a mirror of metallic As will
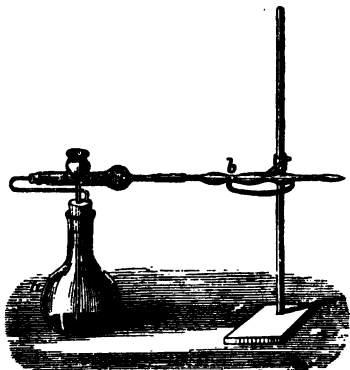
FIG. 63.—Marsh's test for arsenic.

be formed on it; obtain two of these mirrors. A similar mirror will also be deposited within the tube, just beyond the point where the heat has been applied. Add to the mirror a drop of a solution of sodium hypochlorite (NaClO) — the mirror is immediately dissolved. (Marsh's test.)

Place in a test-tube some pure Zn and KHO, with a little water; add a very small quantity of the As solution; then cover over the top of the tube with a piece of filter paper moistened with $AgNO_3$, and heat very gently—the paper is blackened through the decomposition of $AgNO_3$ by AsH_3. (Fleitmann's test.)

ARSENIC COMPOUNDS.—A solution of potassium arsenate (K_3AsO_4) may be used.

Dry. Same as those of arsenious compounds.

Wet. H_2S produces a ppt. from acidulated solution with extreme slowness. The ppt. consists of As_2S_5, hence the H_2S has to reduce the arsenic compound to an arsenious one. Heat the solution with H_2SO_3 until the smell of SO_2 disappears; this readily effects the reduction to the arsenious state; then add H_2S—a yellow ppt. of As_2S_3 is immediately produced.

The greatest care must be taken in all experiments on As, as its compounds are intensely poisonous; small quantities should be used, and the experiment performed either in a stink-cupboard or where there is a good draught of air.

ANTIMONY.—The fused oxy-sulphide may be used for the dry reactions, and a solution of the chloride $SbCl_3$ for the wet.

Dry. Heated gently on charcoal in reducing flame with Na_2CO_3 and KCy—a brittle white metallic bead is formed; this readily oxidizes with the production of a dense white incrustation.

Wet. H_2S—orange ppt. of Sb_2S_3 insol. in dilute HCl, sol. in NaHO or Am_2S, insol. in $AmHCO_3$.

Much H_2O to solution of $SbCl_3$—white ppt. of SbOCl.

Solution added to apparatus in which H is being generated from Zn and H_2SO_4, as described for As, produces SbH_3, which also deposits a mirror. The Sb mirror is darker in colour, and on the addition of NaOCl does not dissolve. (Distinction from As.)

Sb solution added to Zn and KHO, as in test for As, does not form SbH_3, and consequently there is no blackening of the filter paper moistened with $AgNO_3$.

ALUMINIUM.—Alum, $Am_2Al_2(SO_4)_4$, may be used.

Dry. Strongly ignited on charcoal, allowed to cool, moistened with cobalt nitrate solution, $Co(NO_3)_2$, and again strongly ignited—the residue assumes a blue colour.

When the quantity is very small, the reaction may be performed on a loop of Pt wire. This is specially applicable when testing a ppt.: a portion of the filter containing the ppt. may be cut out and heated on the Pt wire.

Wet. AmHO—white gelatinous ppt. of $Al_2(HO)_6$, slightly sol. in excess, readily sol. in NaHO.

The presence of AmCl in the solution prevents the solution of the ppt. by either AmHO or NaHO.

Am_2S—also ppts. $Al_2(HO)_6$, with evolution of H_2S.

CHROMIUM.— Chrome alum, $K_2Cr_2(S_4O_4)$, may be used.

Dry. One part of a Cr salt mixed with about four parts of Na_2CO_3, and one of KNO_3, fused on Pt foil, produces, on cooling, a yellow mass containing K_2CrO_4. This, on the addition of H_2O, produces a yellow solution, from which acetic acid and lead acetate ppt. yellow $PbCrO_4$.

Heated in borax bead in R.F.—green bead.

Wet. AmHO — green ppt. of $Cr_2(HO)_6$, slightly sol. in excess, re-pptd. by boiling, which drives off the excess of AmHO.

The presence of AmCl prevents the solution of the ppt.

Am_2S—same ppt. of $Cr_2(HO)_6$.

MANGANESE.—Manganese sulphate may be used.

Dry. Heated in borax bead—O.F. amethyst, R.F. colourless bead.

Heated on Pt. foil with Na_2CO_3 and KNO_3 (same quantities as directed for Cr)—dark bluish-green mass.

Wet. Am_2S — yellow (skin-coloured) ppt. of MnS, sol. in HCl, and also in acetic acid.

NaHO—white ppt. of $Mn(HO)_2$, which rapidly oxidizes on exposure to air, and acquires a brown tint.

The ppt. is at first sol. in AmCl, but not so after standing.

AmHO—white ppt. sol. in AmCl.

If this solution be allowed to stand, a brown ppt. of $Mn_2O_2(HO)_2$ is formed. Hence, when members of Group IIIA. are present in a mixture with Mn, a portion of the Mn is also pptd. by AmCl, AmHO.

NICKEL.—Nickel sulphate may be used.

Dry. Heated on charcoal with Na_2Co_3 in reducing flame — greyish residue, which, when treated with water and the soluble portion removed, is slightly magnetic.

Heated in borax bead—in O.F. reddish-yellow when hot, sherry colour when cold ; R.F. grey when cold.

Wet. Am_2S—black ppt. of NiS, slightly sol. in excess to yellow-brown solution, insol. in cold dilute HCl.

H_2S—no ppt. in acid solution.

Am_2CO_3 — green ppt. sol. in excess to greenish - blue solution.

KCy—yellow ppt. of $NiCy_2$ sol. in excess to $(KCy)_2$, $NiCy_2$. This solution is unchanged by boiling, and NaClO ppts. from it on heating, $Ni_2(HO)_6$ which is of a black colour.

The KCy must be free from carbonate and cyanate : the latter may be removed by fusion in a porcelain crucible with powdered charcoal. The KCy solution should be made up only when used : it must be added drop by drop until there is only just the slightest excess; the exact point may be hit by reserving a portion of the nickel solution,

and adding a drop to the solution in KCy so as to produce a very slight ppt., and then filtering. A large quantity of the hypochlorite must be added, and if the Ni solution be very dilute, some little time elapses before the $Ni_2(HO)_6$ is pptd.

Bromine water may be employed instead of NaClO.

COBALT.—Cobalt nitrate may be used.

Dry. Heated in borax bead both in O.F. and R.F.—deep blue bead.

The slightest trace of Co should be taken.

Wet. Am_2S—black ppt. of CoS, insol. in excess and also in HCl.

Am_2CO_3—pink ppt. sol. in excess to red solution

KCy—light brown ppt. of $CoCy_2$ sol. in excess to $(KCy)_2$, $CoCy_2$. This solution, on being boiled, is changed to K_3CoCy_6, in which neither NaClO nor Br water produces a ppt.

This affords a method of separating Ni from Co. Make a mixture of the solutions of the salts of these two metals and separate them by this method. Boil the dissolved cyanides for two or three minutes, and then cool before adding the NaClO, after which again gently warm and allow to stand.

BARIUM.—Barium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame — a green coloration.

Flame colorations are best seen with the chlorides.

Wet. Am_2CO_3 in presence of AmHO —white ppt. of $BaCO_3$ sol. in HCl or acetic acid.

$CaSO_4$—white ppt. of $BaSO_4$ even from very dilute solutions.

K_2CrO_4—yellow ppt. of $BaCrO_4$ from dilute solutions, sol. in HCl, but insol. in acetic acid.

STRONTIUM.—Strontium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a crimson flame coloration.

Wet. Am_2CO_3 in presence of AmHO—white ppt. of $SrCO_3$ sol. in HCl or acetic acid.

$CaSO_4$—white ppt. of $SrSO_4$, but only after standing some time, insol. in boiling saturated solution of Am SO_4 with AmHO.

K_2CrO_4—no ppt.

MAGNESIUM.—Magnesium sulphate may be used.

Dry. Strongly ignited òn charcoal, allowed to cool, moistened with Co(NO$_3$)$_2$ and again strongly ignited—the residue assumes a rose-pink colour.

Wet. AmHO—white ppt. of Mg(HO)$_2$ sol. in AmCl.

Na$_2$HPO$_4$ in presence of AmCl and AmHO—white crystalline ppt. of MgAmPO$_4$ sol. in HCl and also acetic acid.

SODIUM.—Sodium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—an intense golden-yellow flame coloration. Viewed through blue glass, the yellow flame is invisible.

This enables K to be detected in the presence of Na.

Wet. Almost all the sodium salts are soluble, and therefore no good wet reaction is applicable.

FURTHER REACTIONS OF THE ACIDS.

The acids do not admit of being so readily arranged in groups as the metals ; the following classification will, however, be found to be a help in studying their reactions.

Group I.—Acids whose salts are decomposed by gently heating with dilute HCl, and which evolve a characteristic gas or vapour :—**Carbonic acid** and **sulphuretted hydrogen.**

Group II.—Acids whose salts are decomposed by heating with concentrated H^{2}SO$_4$, and which evolve a characteristic gas or vapour :—**Nitric, chloric, hydrochloric, hydrobromic, hydriodic,** and **hydrofluoric acids.**

Group III.—Acids whose salts evolve neither gas nor vapour on being treated with H$_2$SO$_4$:—**Sulphuric, silicic, phosphoric,** and **boric acids.**

SULPHURETTED HYDROGEN, H$_2$S.—Ferrous sulphide may be used.

Dry. Certain sulphides are decomposed on being treated in a closed tube, S being deposited ; this reaction is characteristic of sulphides. Others, on being heated in an open tube, are oxidized ; an oxide of the metal remains, and SO$_2$ is evolved, which may be recognized by its smell.

Wet. HCl added to the powdered salt and gently warmed —many sulphides evolve SH$_2$, recognized by its odour and property of blackening paper dipped in a solution of lead acetate.

Others, as As_2S_3, are not decomposed : these, on being warmed with aqua regia, are in part oxidized to sulphates; another portion of the metal forms a chloride, and free S is liberated in the plastic condition. The solution must be diluted and tested for H_2SO_4 by $BaCl_2$.

CHLORIC ACID, $HClO_3$. —Potassium chlorate may be used.

Dry. Heated in tube—all chlorates are decomposed, evolving either O or a mixture of Cl and O.

Heated on charcoal—chlorates deflagrate. Chlorates may be recognized indirectly by their forming, in most instances chlorides on ignition.

Wet. Heated gently with conc. H_2SO_4—greenish yellow explosive gas (Cl_2O_4) is evolved.

A very small quantity of both the chlorate and the acid should be taken ; the quantity of $KClO_3$ should not be larger than a pea ; some half-dozen drops of acid are sufficient. The mouth of the tube, while being heated, should be turned from the operator.

HYDROBROMIC ACID, HBr.—Potassium bromide may be used.

Wet. Heated gently with conc. H_2SO_4—pungent fumes of HBr, together with free Br vapour, recognized by its deep red colour and characteristic odour, are evolved.

Heated with conc. H_2SO_4 and MnO_2—Br is evolved.

Cl water—Br is liberated, and may be dissolved by CS_2, to which it imparts a deep sherry-red tint.

$AgNO_3$—light yellow ppt. of AgBr, difficultly soluble in AmHO.

HYDRIODIC ACID, HI.—Potassium iodide may be used.

Wet. Heated gently with conc. H_2SO_4—gaseous I, recognized by its violet colour, and HI fumes are evolved.

Heated with conc. H_2SO_4 and MnO_2—I is evolved.

Br water—I is liberated, and may be dissolved by CS_2, to which it imparts a characteristic violet colour.

In making this test add the Br water carefully, drop by drop, then add the CS_2, shake up, and observe whether, after standing, the CS_2 is coloured.

$AgNO_3$—light yellow ppt. of AgI insol. in AmHO.

HYDROFLUORIC ACID, HF.—Calcium fluoride may be used.

Wet. Heated gently with conc. H_2SO_4—pungent acid fumes

evolved, somewhat resembling those of HCl ; a glass rod moistened with water inserted in the tube becomes coated with a film of SiO_2. The glass of the tube is corroded by the HF evolved.

Heated gently in leaden capsule with H_2SO_4—a piece of glass which has been coated with wax and then some characters inscribed with the point of a needle being used as a cover, the glass is eaten away (etched) where the wax has been removed.

SILICIC ACID, H_4SiO_4.—Sodium silicate may be used.

Dry. Heated in a microcosmic salt bead (made in the same way as a borax bead)—silicates are decomposed, and the SiO_2 floats about undissolved in the bead while hot.

Wet. HCl—in conc. solution, gelatinous ppt. of H_4SiO_4.

If the solution be dilute, the H_4SiO_4 does not separate.

The solution being rendered distinctly acid with HCl, and evaporated to complete dryness ; then treated with a few drops of conc. HCl and H_2O and heated—an insol. residue of SiO_2 remains.

AmCl—white gelatinous ppt. of H_4SiO_4.

By fusion with Na_2CO_4 or fusion mixture insol. silicates may be decomposed, sodium or potassium silicates being formed.

PHOSPHORIC ACID, H_3PO_4.—Sodium phosphate may be used.

Wet. AmCl, AmHO, and $MgCl_2$ to alkaline phosphates (*i.e.* phosphates of K, Na, Am)—white crystalline ppt. of $MgAmPO_4$.

Am_2MoO_4 (ammonium molybdate) in presence of excess of HNO_3—yellow ppt. on heating *gently*.

. To the solution tested an equal volume of conc. HNO_3 should be added, and then a volume of Am_2MoO_4 equal to that of the other two together.

All phosphates, except those of the alkalies, are insol. in H_2O ; the remainder are sol. in acids, but are reprecipitated on rendering the solution alkaline. From this property of phosphates, they are, if present in a mixture, pptd. with the members of Group III. on the addition of AmCl and AmHO. Under these circumstances the H_3PO_4 is removed before the examination of the ppt. for the ordinary members of the group is made. Directions are given in a special table for this elimination of H_3PO_4.

If H_3PO_4 is known to be absent from a substance being analyzed, the special tests and methods necessary when it may possibly be present can be omitted.

BORIC ACID, H_3BO_3.—Sodium borate may be used.

Dry. Most borates contain a large quantity of water of crystallization, and therefore swell up when heated.

Wet. Acidulated with conc. H_2SO_4 and alcohol (methylated spirits) added—the mixture on being inflamed burns with a green flame.

The reaction may be performed in a small evaporating basin.

Cu and Ba salts have green flame colorations, and in their presence the following modification of this reaction should be used.

Fit a 2-oz. flask with a cork, through which a glass jet is passed. Put the borate with H_2SO_4 and alcohol in the flask, replace the cork, and apply heat. Set fire to the vapour as it issues from the jet—it burns with a green flame coloration.

Cu and Ba do not affect the flame when produced in this manner.

ORGANIC ACIDS.

HYDROCYANIC ACID, HCN or HCy.[1]—Potassium cyanide may be used.

Dry. Cyanides of the heavy metals, as $HgCy_2$, are decomposed by heat, with the evolution of Cy, which burns with a purple flame.

Cyanides evolve their N as NH_3 when heated with sodalime.

KCy and NaCy are not decomposed by ignition, but in the presence of air are rapidly converted into KCyO and NaCyO (cyanates). Owing to the avidity with which they combine with O they are valuable reducing agents.

Wet. Heated with HCl—all cyanides evolve HCy, having a characteristic odour of bitter almonds. Hold a watch-glass, on the bottom of which a drop of SAm_2 has been placed, in the gas thus evolved from a cyanide—AmCyS is formed; allow

[1] Cyanogen, CN, is such an important compound radical that it has received the special symbol " Cy."

the excess of SAm_2 to evaporate, and wash the AmCyS into a test-tube, add a single drop of Fe_2Cl_6—reddish coloration.

$AgNO_3$—white ppt. of AgCy readily sol. in AmHO.

OXALIC ACID, $H_2C_2O_4$.—Ammonium oxalate may be used.

Dry. Oxalic acid sublimes on being heated, forming dense white fumes; the sublimate crystallizes in long needles, generally radiating from a common centre. Oxalates are decomposed into carbonates or oxides, with evolution of CO and CO_2.

Wet. Heated with conc. H_2SO_4, CO and CO_2 are evolved ; the mixture does not blacken.

$CaCl_2$ or $CaSO_4$, from ammoniacal or acetic acid solution— white ppt. of CaC_2O_4, readily soluble in HCl or HNO_3. The ppt., on being evaporated to dryness and raised to a dull red heat, is converted into $CaCO_3$, which effervesces on the addition of HCl.

FORMIC ACID, $HCHO_2$.—Sodium formate ($NaCHO_2$) may be used.

Dry. Formates, on being heated, split up into carbonates, oxides, or metals, with evolution of H_2, CO, and CO_2, and separation of C.

Wet. On addition of conc. H_2SO_4—characteristic smell of $HCHO_2$; on heating, CO is evolved without blackening or evolution of CO_2.

$HgCl_2$ or $Hg_2(NO_3)_2$—grey ppt. of Hg, CO_2 being evolved.

Fe_2Cl_6—in neutral solution, a deep red coloration ; addition of HCl changes the colour to yellow. On boiling, the solution becomes colourless, with separation of the iron as a basic formate.

ACETIC ACID, $HC_2H_3O_2$.—Sodium acetate may be used.

Dry. Acetates are decomposed on the application of heat ; an inflammable liquid termed acetone, having a characteristic odour, is evolved. The metal remains as either carbonate or oxide, or in the metallic state mixed with C.

Acetates, heated with a small quantity of As_2O_3 evolve cacodyl, having a most disgusting odour.

Wet. Heated with H_2SO_4—characteristic smell of acetic acid is evolved. On heating with conc. H_2SO_4 and a single drop of alcohol (not methylated spirit), acetic ether, having a characteristic and pleasant smell, is yielded.

Fe_2Cl_6—reaction similar to that with formates.

BENZOIC ACID, $HC_7H_5O_2$.—Ammonium benzoate may be used.

Dry. Heated in a tube, benzoic acid sublimes and recondenses in acicular crystals, an incense-like odour is evolved ; heated on platinum foil, the acid burns with a bright smoky flame.

Wet. Heated with conc. H_2SO_4, benzoates produce neither blackening nor evolution of SO_2.

Fe_2Cl_6—in neutral solution a yellowish ppt. of ferric benzoate, soluble in excess.

$CaCl_2$ and alcohol—no ppt.

SUCCINIC ACID, $H_2C_4H_4O$.—Ammonium succinate may be used.

Dry. Heated in a tube, the acid sublimes and re-condenses as long and very delicate needles, fumes are evolved which produce violent coughing ; heated on platinum foil, the acid burns with a blue smokeless flame.

Wet. Heated with conc. H_2SO_4—no reaction.

F_2Cl_6—in neutral solutions a brownish-red ppt. which darkens in colour on adding AmHO.

$BaCl_2$ and alcohol—white ppt.

TARTARIC ACID, $H_2C_4H_4O_6$.—Sodium potassium tartrate (Rochelle salt) may be used.

Dry. Heated in a tube, the acid and tartrates are decomposed, with separation of C and evolution of odour of burnt sugar.

Wet. Heated with conc. H_2SO_4—SO_2, CO_2, and CO are evolved, and C separates and blackens the mixture.

KCl—in solution acidulated with acetic acid—white crystalline ppt. of $HKC_4H_4O_6$.

$CaCl_2$—white ppt. of calcium tartrate, sol. in acids, cold NaHO and ammonic salts, but insol. in AmHO.

CITRIC ACID, $H_3C_6H_5O_7$.—Citric acid may be used.

Dry. Heated in a tube, pungent acrid fumes are evolved, and C remains.

Wet. Heated with conc. H_2SO_4—CO and CO_2 are evolved. After *prolonged* heating the mixture blackens, and SO_2 is given off.

$CaCl_2$ added to solution exactly neutralized with NaHO—no ppt. in the cold (except on long standing) ; on boiling—white ppt. of calcium citrate.

TABLES FOR THE ANALYSIS OF UNKNOWN INORGANIC SUBSTANCES CONTAINING ALL OR ANY OF THE FOREGOING BASES AND ACIDS.

Refer back to the directions for analysis given on p. 344.

PRELIMINARY EXAMINATION BY THE DRY WAY.

I. HEAT A LITTLE OF THE POWDERED SUBSTANCE IN A TEST-TUBE OR PIECE OF SMALL COMBUSTION TUBING CLOSED AT ONE END AND A SMALL BULB BLOWN.

RESULT.	DEDUCTION. Presence of—
NH_3 is evolved . . .	**Am** salts.
Nitrous fumes evolved . .	**Nitrates** of the heavy metals.
A sublimate is formed.[1]	
White	**Am** salts, $HgCl_2$, Hg_2Cl_2, As_2O_3, $CdBr$. At a red heat,– Sb_2O_3.
Reddish-brown drops . .	**Sulphur.**
Yellow . . .	As_2S_3, HgI_2. The latter turns red on being rubbed.
Black	HgS; turns red on being rubbed.
	In case of white sublimate. Test for Am by heating a little of the original substance with solution of NaHO—NH_3 evolved. **Am is present.**
	Heat some of the original substance in a small tube with five times its weight of fusion mixture—solid metallic sublimate—**As.** Sublimate of liquid globules—**Hg.**
Solid metallic sublimate . .	**As.**
Sublimate of liquid globules .	**Hg.**

[1] If there be no sublimate or other principal reaction, the confirmatory tests, etc., under the heading of "Deduction" are to be omitted.

II. HEAT SOME OF THE SUBSTANCE ON CHARCOAL WITH
THE BLOWPIPE IN OXIDIZING FLAME.

RESULT.	DEDUCTION. Presence of—
The substance deflagrates .	**Nitrates, Chlorates.**
An infusible residue remains.	
White	**ZnO, Al₂O₃, SiO₂, BaO, SrO, CaO, MgO**, etc.

$ZnO, Al_2O_3, SiO_2, BaO, SrO, CaO, MgO$, etc.

> Moisten the white residue, when cold, with $Co(NO_3)_2$, and ignite strongly.
> Blue mass—Al_2O_3.
> Pink mass—MgO.
> Green mass—ZnO.

| Residue coloured . . | **CuO, MnO, NiO, CoO, Fe₂O₃, Cr₂O₃.** |

$CuO, MnO, NiO, CoO, Fe_2O_3, Cr_2O_3$.

> Heat a portion of the substance in borax bead—
> O.F. green while hot, blue when cold—**Cu.**
> O.F. amethyst bead, R.F. colourless—**Mn.**
> O F. sherry-red—**Ni.**
> In both flames, dark blue bead—**Co.**
> O.F. pale yellow, R.F. olive-green bead—**Fe.**
> In both flames, green bead—**Cr.**
> Test specially for **Mn** and **Cr** by heating with fusion mixture and KNO_3 on Pt foil.

III. Heat the substance with fusion mixture in the reducing flame.

Result.	Deduction. Presence of—
An incrustation is formed without metallic bead.	
White, with garlic odour .	**As** compounds.
Yellow while hot, white when cold	**Zn.**
Reddish brown, deposited some distance from assay	**Cd.**
A metallic bead is formed .	**Ag, Pb, Cu, Bi, Sn, Sb.**
The bead is white, malleable, and not coated with oxide	**Ag**; dissolves readily in HNO_3.
Soft bluish-white malleable bead which marks paper; yellow incrustation . .	**Pb.**
Small red malleable beads with black coating of oxide . . .	**Cu.**
Brittle yellowish-white bead, with dark orange incrustation while hot, light yellow when cold . .	**Bi.**
Soft malleable yellowish-white bead, with incrustation yellow when hot, white when cold.	**Sn**; does not dissolve in HNO_3, but is changed into white $Sn_5O_5(HO)_{10}$.
Brittle white bead, with dense white fumes, which form a white incrustation	**Sb.**

IV. DIP A CLEAN Pt WIRE, MOISTENED WITH HCl, INTO
    SOME OF THE SUBSTANCE, AND HEAT IN THE BUNSEN
    FLAME.

RESULT.	DEDUCTION. Presence of—
Green flame coloration . .	Cu, Ba, H₃BO₃ ; with Cu, bluish-green.
Crimson ,, ,, · .	Sr.
Yellowish-red ,, ,, · .	Ca.
Golden Yellow ,, ,, · .	Na.
Violet ,, ,, · .	K. In the presence of Na, test flame coloration for K, with blue glass.

As before stated, the preliminary examination must on no account be omitted. The remarks given on p. 346 apply also here.

The following are the most important and characteristic reactions of the preliminary examination :—

Experiment I.—The presence or absence of salts of Am, Hg, and As.

The presence of nitrates of the heavy metals.

Experiment II.—The presence or absence of nitrates and chlorates.

The presence or absence of Mn, Co, and Cr.

Experiment III.—Confirmation of the presence of As.

The presence of Zn, Cd, Bi, and Sb.

The borax bead and incrustation reactions of some metals are particularly liable to be obscured by the others—thus Co masks all other bead reactions ; and one incrustation may hide another. By watching carefully, two incrustations may often be detected, as one metal may be more easily reduced than· another, and so form an incrustation first, which may afterwards be overlaid.

Experiment IV.—The presence or absence of Sr, Na, and K.

When more than one of the metals which colour a flame are present, alternate flashes of each may sometimes be seen.

If the substance be metallic, the presence or absence of Hg and As may be learned from Experiment I. Nos. II. and IV. may be omitted. In No. III. heat a fragment of the metal and observe if any characteristic incrustation be observed.

EXAMINATION IN THE WET WAY.

If the substance be solid, proceed to make a solution, remembering that the substance must first be finely powdered.

I. If the substance is metallic, add dilute HNO_3; and then, if necessary, the concentrated acid; heat gently. The substance either entirely dissolves, or leaves a white residue of $Sn_5O_5(HO)_{10}$ or Sb_2O_5.

Wash the residue and boil with a concentrated solution of tartaric acid; Sb_2O_5 is soluble, test the solution by H_2S for Sb. Test the insoluble residue for Sn by reaction on charcoal.

Evaporate the solution in HNO_3 until the nitrates begin to crystallise out; then add water, and again evaporate down. By this treatment the free acid is driven off. The solution may then be examined in the ordinary way.

II. If the substance is non-metallic, test its solubility in the following reagents in the order given :—

1. H_2O. Heat a small portion of the substance with H_2O in a test-tube; if it be soluble, pass on to analysis. If it dissolve on boiling and re-ppts. on cooling, or is insoluble, pass on to trying. HCl.

2. HCl. First heat a small portion gently with the dilute acid; if not readily dissolved, try concentrated HCl, and boil for some time if necessary; this will dissolve out almost all that is soluble. Filter off the solution.

3. HNO_3. If the substance contains either Hg, Ag, or Pb, use HNO_3 as a solvent instead of HCl. As oxides of Sn or Sb would be insoluble in HNO_3 wash the residue and treat with HCl; mix the two solutions together; any ppt formed will belong to Group I.

4. Aqua regia. Digest any insoluble residue from 2 or 3 with aqua regia; dilute and filter. Note whether globules of plastic S separate out; in which case a sulphide is present. Evaporate down the acid solutions until almost free from acid before proceeding to analysis; HNO_3 in particular should be carefully driven off.

$PbCl_2$ is sol. in hot H_2O and acids, and crystallises out as the liquid cools.

If a ppt. is produced on diluting the acid solution, it probably consists of an oxy-compound of Bi or Sb (as BiOCl). It readily dissolves on the addition of a little more acid. The dry examination will have proved the presence or absence of these metals.

III. A residue insoluble in acids remains. The number of such substances is but few; the following are the most important :—

SiO_2, and most silicates, Ag and Pb chlorides; Pb, Ba, Sr, and Ca sulphates; native and ignited compounds of Al_2O_3, Fe_2O_3, Cr_2O_3, SnO_2, and some native fluorides.

Take about three grammes of fusion mixture and melt it in a platinum capsule over the foot-blowpipe flame; raise to a bright red heat. Take about half a gramme of the very finely-powdered substance and add it in small quantities at a time to the liquid fusion mixture; on each addition an effervescence follows; wait until all action is over before adding more. When the whole has been introduced and thus decomposed, allow it to cool. The blowpipe heat must be maintained during the whole of this operation.

Should there be any reducible metal present, a porcelain crucible must be used instead of platinum; but in this case traces of SiO_2 and Al_2O_3 will be found from the crucible.

By fusion in this way the metal is obtained either as carbonate, oxide, or in the free state. The acid will have formed a potassium or sodium salt with the fusion mixture. When cold, boil up with water. The aqueous solution must be tested for acids. Filter off, and wash the residue thoroughly; dissolve in HCl, and examine the solution for the base. Should there still be any insoluble residue, the substance has not been entirely decomposed by the fusion mixture.

It is impossible by this method to determine whether or not any alkalies are present in the insoluble substance. To examine for alka-lies, proceed in the following manner :—

Take not more than 0·5 grammes of the substance; mix with 0·5 grammes of pure AmCl and 4 grammes of pure precipitated $CaCO_3$; mix thoroughly, and heat in a platinum crucible with a small Bunsen flame. The crucible should be placed obliquely, and the heat applied to the upper part of the crucible first, working toward the bottom. The heat should then be increased, and finally the mass ignited strongly for half an hour with the foot-blowpipe. Extract with successive small quantities of hot H_2O and filter : the filtrate contains the alkalies, as chlorides, and also $CaCl_2$. Remove the Ca by ammonium oxalate and examine the filtrate for Na and K in the usual manner.

The solutions obtained by decomposing an insoluble residue by fusion mixture must be examined separately from the aqueous or acid solutions.

Proceed to examine a portion of the solution obtained by Table A.

Table A, for the separation of the bases into Groups.

To the original solution add HCl until it no longer produces a precipitate.

Dilute the filtrate, and pass SH₂ gas until the solution smells strongly of the gas. Heat gently.

The ppt. may contain	The ppt. may contain	Boil the filtrate till free from SH₂. Test a small portion for H_3PO_4, by HNO_3 and Am_2MoO_4.. To another small portion add AmCl and AmHO; if there is no ppt. add these reagents to the main portion of the filtrate, and at once proceed to pass SH₂ gas or add SAm₂. But if there be a ppt. add to the main portion of the filtrate a few drops of conc. HNO_3 and evaporate to complete dryness: add a little conc. HCl and then heat with H_2O; the substance either dissolves completely or leaves a residue of SiO_2, which must be filtered off. Two cases now present themselves—1, H_3PO_4 is absent; 2, H_3PO_4 is present.				To the filtrate add SH₂ gas or SAm₂ in slight excess. Heat gently.	To the filtrate add AmHO and Am₂CO₃. Heat gently and allow to stand for a few minutes.	The solution may contain
$AgCl$, white,	HgS, black.							Mg
$PbCl_2$ „	PbS, „							K
Hg_2Cl_2 „	Bi_2S_3, „	To the remainder of the solution, in absence of SiO_2, or to the filtrate from SiO_2, when present, add AmCl and AmHO in slight excess, and immediately boil until it no longer smells of NH_3.						Na
	CuS, „							
Filter and wash thoroughly with *cold* H_2O.	CdS, yellow.	1, H_3PO_4 is absent.	2, H_3PO_4 is present.	The ppt. may contain			
	SnS, brown.	The ppt. may contain	The ppt. may contain	ZnS, white.		The ppt. may contain	Group V.
	SnS_2, yellow.	$Fe_2(HO)_6$, reddish brown.	$Fe_2(HO)_6$, reddish brown.	MnS, tawny yellow.		$BaCO_3$, white.	Examine by Table H.
	Sb_2S_3, orange.	$Cr_2(HO)_6$, green.	$Cr_2(HO)_6$, green.	NiS, black.		$SrCO_3$, „	
Group I.	Sb_2S_5, „	$Al_2(HO)_6$, white.	$Al_2(HO)_6$, white,	CoS, „		$CaCO_3$, „	
Examine by Table B.	As_2S_3, yellow.		and also the phosphates of all or any of the following metals—	Filter and wash.		Filter and wash.	
	Filter and wash.	Filter immediately and wash.	Fe, Cr, Al, Zn, Mn, Ni, Co, Ba, Sr, Ca, and Mg.	Group III. B.		Group IV.	
	Group II.	Group III. A.	Filter immediately and wash.	Examine by Table F.		Examine by Table G.	
	Examine by Table C.	Examine by Table D.	Group III. A with H_3PO_4.				
			Examine by Table E.				

Notes on Table A.

The separation into groups is based on the insolubility of the chlorides and other salts formed by the addition of various reagents; they are then removed by filtration, each ppt. being thoroughly washed.

Before proceeding to add the following group reagent, be sure that the preceding one has been added in excess. If the ppt. subsides readily, leaving a clear solution on the top, a drop of the reagent should be carefully added; if the liquid remains clear, go on to the next group; if a trace of ppt. forms, more of the reagent must be added, until a drop no longer produces a ppt. In some cases it will be necessary to filter a portion of the solution and make this test on the filtrate. An excess of SH_2 and AmHO may be recognised by their odour.

In addition to the metals of Group I., HCl may ppt., from an alkaline solution, As_2S_3, Sb_2S_3, SnS, and also H_4SiO_4 (gelatinous ppt.) Note the colour of the ppt. $BaCl_2$ may also be pptd. from a saturated solution of a baric salt, but is dissolved readily on the addition of a little H_2O.

SH_2 in the presence of oxidising agents produces a ppt. of S in the second group; it may be recognised by its being white and remaining suspended in the liquid. It does not interfere with the reaction of the metals, and may therefore be neglected.

The solution must not be too acid, as CdS is not pptd. in the presence of a large excess of HCl.

AmCl and AmHO ppt. not only the metals of Group III. A, but also phosphates of the metals of Groups III. and IV., and H_4SiO_4, if present. A small portion only of the filtrate of Group II. is first tested; should there be a ppt., it is necessary to test for and remove the H_4SiO_4, if present. (Except in very few cases, SiO_2 will not be found when the substance has completely dissolved in H_2O.) The presence of H_3PO_4 requires special steps to be taken for its removal. The filtrate is boiled with HNO_3 in order to oxidise any ferrous salts present.

The ppt. in Group III. A must be filtered and washed immediately, because Mn, if present, is after a time oxidised into $Mn_2O_3(HO)_2$, and is then found in the ppt. If Mn be present in the substance, traces are always pptd. with the metals of Group III. A; these, however, may be neglected.

NiS is somewhat soluble in SAm_2, to which it imparts a yellowish-brown tint. Under these circumstances, after filtering off the ppt., evaporate the filtrate nearly to dryness, add H_2O, again filter, and test

the ppt. specially for Ni by the borax bead reaction. Add Group IV. reagents to this second filtrate.

Special care must be taken not to boil Group IV. solution, to which the reagents have been added, as thereby $CaCO_3$ is in part reconverted into $CaCl_2$, and passes over into the fifth group.

Table B, for the examination of Group I. precipitate.

Transfer the ppt. to a test-tube, add water, boil and filter while hot. Wash the ppt. with boiling water.		
RESIDUE.— Add AmHO in excess, and filter.		SOLUTION.—Add K_2CrO_4 —yellow ppt. of $PbCrO_4$.
RESIDUE is blackened, and consists of NH_2Hg_2Cl. Confirmed by dry reactions. **Hg is present as a mercurous salt.**	SOLUTION.—Add HNO_3 —a white curdy ppt. of AgCl, turning purple on exposure to light. Confirmed by dry reaction. **Ag is present.**	Confirmed by dry reaction. **Pb is present.**

The separation of the metals of this group depends on solubility of $PbCl_2$ in hot H_2O; the solubility of AgCl in AmHO, and the insolubility of Hg_2Cl_2 in that reagent.

The absence of the reactions given may be taken as evidence of the absence of the particular metals. Thus, if the ppt. left no residue on being boiled with water, AgCl and Hg_2Cl_2 cannot be present; or if the water dissolved out nothing, $PbCl_2$ must be absent.

If a portion of the $PbCl_2$ solution be set aside to cool, $PbCl_2$ will crystallise out.

Table C, for the examination of Group II. precipitate.

Thoroughly wash the ppt. with water, to which a few drops of SH₂ solution have been added, transfer the ppt. to a test-tube, digest with NaHO and filter.

RESIDUE may contain HgS, PbS, Bi₂S₃, CuS, and CdS. Note the colour, if dark coloured, wash, boil with conc. HNO₃. If yellow CdS only is present, dilute and filter.

SOLUTION may contain the sulphides of Sb, Sn, and As. Re-ppt. by adding HCl in slight excess; filter, wash and digest with one or two fragments of solid ammonium carbonate (sesquicarbonate), and filter.

RESIDUE branch

SOLUTION.—Add H₂SO₄ and equal volume of alcohol (methylated spirit); filter.

RESIDUE is black, and consists of HgS. Confirmed by dry reaction.		**Hg is present as a mercuric salt.**
PRECIPITATE consists of PbSO₄.	Confirm by dissolving the ppt. in boiling ammonium acetate, and adding K₂CrO₄,—yellow ppt. of PbCrO₄.	**Pb is present.**

FILTRATE.—Boil off alcohol, add AmHO in excess, boil and filter.

PRECIPITATE consists of Bi(HO)₃.	Confirm by dissolving in the smallest possible quantity of HCl, and then adding H₂O,—white ppt. of BiOCl	**Bi is present.**

FILTRATE—if blue, Cu is present. If not Cu is absent. If Cu is present, add solution of KCy drop by drop until the blue colour just disappears. Add SH₂, solution.

PRECIPITATE is yellow, and consists of CdS.	Confirmed by dry reaction.	**Cd is present.**
FILTRATE will contain CuCy₂ if Cu is present.	Confirmed by acidulating with HCl, boiling off HCy, and adding K₄FeCy₆,—brown ppt. of Cu₂FeCy₆.	**Cu is present.**

SOLUTION branch

RESIDUE may contain Sb₂S₃ and SnS or SnS₂. Dissolve in boiling conc. HCl, dilute with H₂O, introduce a piece of Pt foil and a fragment of Zn.

Sb produces a black stain on the Pt: dissolve this off with H₂O₂, evaporate down and add SH₂,—orange ppt. of Sb₂S₃.	Confirmed by dry reaction on charcoal. (May be further confirmed by Marsh's test.) **Sb is present.**
Sn is deposited on the Zn: dissolve by boiling with conc. HCl with the aid of a piece of Pt foil introduced. Dilute with H₂O and add HgCl₂—white ppt. of Hg₂Cl₂ or grey ppt. of Hg.	**Sn is present.**

SOLUTION may contain As₂S₃. Acidulate with HCl — bright yellow ppt. of As₂S₃ is re-pptd. Confirmed by dry reactions. (Fleitmann's and Marsh's tests may be used as further confirmatory tests if thought desirable. **As is present.**

The separation of the metals of this group depends (1st) on the solubility of the sulphides of Sb, As, and Sn in NaHO, while the others are insoluble. The As_2S_3 is soluble in hydric ammonic carbonate (solution of the solid carbonate, $AmHCO_3$), and is thus separated from the sulphides of Sn and Sb. These are then dissolved in HCl; on Pt and Zn being introduced, a voltaic action is set up, and this causes the deposition of the Sb on the Pt; the Sn is deposited on the Zn; both are then recognised by confirmatory tests.

The sulphides insoluble in NaHO are soluble in HNO_3, with the exception of HgS. This reaction therefore enables us to separate this sulphide. Any traces of Pb are removed by precipitation with H_2SO_4 and alcohol (most sulphates are less soluble in alcohol and H_2O than H_2O alone). $Bi(HO)_3$ is insoluble in excess of AmHO; $Cu(HO)_2$ and $Cd(HO)_2$ are soluble. The blue colour of the ammoniacal solution of $Cu(HO)_2$ is a sure test of the presence of Cu. Cu and Cd are both pptd. by KCy, and are both soluble in excess; from this solution SH_2 ppts. CdS, but not CuS; in this way the last two are separated.

S_2Am_2 may be used instead of NaHO for the separation of the sulphides of As, &c. If the presence of HgS is suspected, it is preferable to use S_2Am_2, as HgS is somewhat soluble in NaHO. If NaHO or S_2Am_2 leaves a yellow residue, it can only consist of CdS. To be sure that it is not confounded with S, dissolve in HCl, and filter; add AmHO and SH_2,—CdS is re-pptd. In the absence of the other sulphides, treatment with HNO_3, &c., is of course unnecessary. HNO_3 ppts. S from SH_2; a white ppt., therefore, on treating the mixed sulphides with this reagent may be neglected.

If, from the absence of any blue coloration on the addition of AmHO for the separation of Bi, Cu is known not to be present, proceed at once to test for Cd by adding AmHO in slight excess and SH_2, when Cd will be pptd. as CdS if present.

A careful preliminary examination should reveal with certainty the presence or absence of As, and Sb ought also to be detected if present. This knowledge is of material help in the examination of the ppt. containing As_2S_3, &c. In the known absence of As, treatment with $AmHCO_3$ is unnecessary.

When directions are given to 'digest' a ppt., put the test-tube containing it into a beaker of boiling water. This prevents the temperature of the substance to be digested actually reaching the boiling point.

Table D, for the examination of Group III. A precipitate in the absence of Phosphoric Acid.

Note the colour of the ppt. : if white, $Al_2(HO)_6$ only is present; if coloured green or reddish brown, Cr or Fe is present. Dissolve the ppt. in dilute HCl, add NaHO in excess, boil and filter.		

RESIDUE.—Dry and test for Cr by fusing on Pt foil with fusion mixture and KNO_3. Dissolve in hot H_2O, and filter.		SOLUTION may contain Al : acidulate with HCl, and add a slight excess of AmHO—white gelatinous ppt. of $Al_2(HO)_6$.
RESIDUE. — Dissolve in HCl, and test by K_4FeCy_6—a dark blue ppt. **Fe is present.**	SOLUTION is of a yellow colour through the formation of K_2CrO_4. Confirm by adding $HC_2H_3O_2$ (acetic acid) and lead acetate—yellow ppt. of $PbCrO_4$. Confirmed also by borax bead reaction. **Cr is present.**	**Al is present.**

The separation and detection of the metals of this group depends on the solubility of $Al_2(HO)_6$ in NaHO; the formation of a chromate by fusion of Cr compounds with fusion mixture and KNO_3, while Fe remains in the residue.

To determine whether the Fe is present in the substance as a ferrous or ferric salt, test the original solution in H_2O or HCl by $K_6Fe_2Cy_{12}$ and AmCyS.

Should the group ppt. contain any Mn, the solution after fusion with fusion mixture and KNO_3 will be coloured purple by permanganate. This, although obscuring the yellow colour of the fused mass and its solution, will not interfere with the precipitation of $PbCrO_4$.

It is difficult to obtain NaHO free from alumina. In cases where the detection of Al is very important, NaHO prepared from Na should be used. The student should test the NaHO for Al, and thus he will be able to judge whether his ppt. in this group is more than that afforded by the reagents alone.

Table E, for the examination of Group III. A precipitate in the presence of Phosphoric Acid.

Dissolve the ppt. in slight excess of HCl. Test specially for Fe in small portion by K₄FeCy₆. Add AmHO to the main portion drop by drop until the solution is nearly neutral (this is known by a drop producing a slight ppt. which only just dissolves on shaking the solution) ; add ammonium acetate : if the liquid does not redden, add a single drop of dilute Fe₂Cl₆ solution, or sufficient to produce a slight red coloration. Boil and filter.

PRECIPITATE contains all the H₃PO₄ in combination with Fe, or Al and Cr if present. Wash, boil with excess of pure NaHO, and filter.		FILTRATE may contain any of the metals of Groups III. B and IV. Proceed, as directed in general table A, to add the several reagents for these groups.
RESIDUE.—Dry a portion and fuse on Pt foil with fusion mixture and KNO₃. Dissolve in H₂O, filter if necessary, and add acetic acid and lead acetate to the filtrate — yellow ppt. of PbCrO₄. **Cr is present.**	SOLUTION. — Acidulate with HCl, add AmHO — white gelatinous ppt. of Al₂(PO₄)₃. Confirm by igniting the ppt. on charcoal and treating with Co(NO₃)₂ —blue coloured mass. **Al is present.**	

Ammonium acetate ppts. the phosphates of Al, Fe, and Cr, if present. Should these be absent, Fe₂Cl₆ is added in order to decompose the phosphates of Groups III. B and IV., chlorides of these metals being formed and Fe₂(PO₄)₂ pptd. The Fe₂Cl₆ must be added cautiously, as the phosphate is soluble in excess of Fe₂Cl₆. The slightest excess produces a red coloration, owing to the formation of iron acetate. On boiling, the whole of the iron is pptd. Fe₂Cl₆ being here used as a reagent, Fe must be specially tested for.

The detection of Al depends on the solubility of Al₂(PO₄)₂ in NaHO,

Table F, for the examination of Group III. B precipitate.

Should the filtrate from this ppt. be dark in colour, proceed according to note on Table A. This coloration is a valuable indication of the presence of Ni. Wash the ppt. with water to which a iittle SH₂ has been added. Shake up with cold dilute HCl, and filter.

RESIDUE may contain CoS and NiS.		SOLUTION.—Boil off SH₂ (filter if necessary), add excess of NaHO, heat and filter.	
Co will have been detected by the deep-blue colora-tion of the borax bead in dry reac-tion. Confirm by repeat-ing this test with a trace of the resi-due—blue colora-tion. **Co is present.**	Ni will have been indicated by solu-bility of NiS. In the presence of Co, dissolve the residue by boiling with conc. HCl and a small fragment of KClO₃, boil until the chlorous odour disappears, nearly neutralise with Na₂CO₃, add KCy drop by drop until the ppt. first formed is just redissolved, boil briskly, then add large quantity of NaClO solution or Br water, and warm gently—black ppt. of Ni₂(HO)₆. Confirm by testing the ppt. for Ni in borax bead. **Ni is present.**	PRECIPITATE is white, and con-sists of Mn(HO)₂ but rapidly turns brown. Confirm by fusion on Pt foil with fusion mixture and KNO₃,—blue residue. **Mn is present.**	FILTRATE.—Add SH₂—white ppt. of ZnS. Confirm by ignit-ing the ppt. on charcoal and then heating with Co(NO₃)₂ —green mass. **Zn is present.**

The separation of the metals of this group depends, first on the insolubility of CoS and NiS in cold dilute HCl. In the presence of Co, which is detected in the preliminary examination by the borax bead reaction, Ni is separated by ppting. the metals as cyanides, and then dissolving the ppt. in excess of KCy: from this solution NaClO ppts. Ni₂(HO)₆ but not Co.

The separation of Mn and Zn depends on the solubility of Zn(HO)₂ and insolubility of Mn(HO)₂ in an excess of NaHO.

Should the group ppt. be light in colour NiS and CoS are absent ; if no Co reaction has been obtained in the dry examination, a black ppt. can only be NiS ; separation by KCy and NaClO is then unneces-sary. It is well, however, to make sure of the absence of Co by testing the group ppt. by the borax bead reaction.

Table G, for the examination of Group IV. precipitate.

Wash the ppt., dissolve in the smallest possible quantity of acetic acid. Test a small portion of this solution for Ba by adding K_2CrO_4: if absent, test another small portion for Sr by flame coloration on Pt wire, and also by adding $CaSO_4$ to a portion and allowing it to stand for some minutes; if Ba and Sr are absent, the ppt. must be $CaCO_3$. Confirm by largely diluting a portion of the solution with H_2O and adding ammonium oxalate—white ppt. of calcium oxalate. In the presence of Ba, add K_2CrO_4 in slight excess to the main portion of the acetic acid solution, and filter.

PRECIPITATE is yellow, and consists of $BaCrO_4$. Wash and confirm by flame coloration — green. **Ba is present.**	FILTRATE.—Add dilute H_2SO_4, filter and wash. Digest the ppt. for some time with AmHO and a saturated solution of Am_2SO_4. Filter.	
	RESIDUE consists of $SrSO_4$. Confirm by moistening with HCl and testing flame coloration —crimson. **Sr is present.**	SOLUTION.—Dilute largely and add ammonium oxalate—white ppt. of calcium oxalate. **Ca is present.**

The separation depends on the insolubility of $BaCrO_4$ in acetic acid, and the solubility of $CaSO_4$ and the insolubility of $SrSO_4$ in Am_2SO_4.

$BaCrO_4$ is very difficult to filter; the best plan is to use for this purpose a 'Swedish' filter paper, as this make has much finer texture.

In making flame tests, the yellowish red Ca coloration must not be confounded with the rich crimson of Sr.

Table H, for the examination of Group V. solution.

To a portion of the solution add Na_2HPO_4 and shake well—a white crystalline ppt. of $MgAmPO_4$—Mg is present. Mg, if present, must be removed as follows :—Evaporate the solution to dryness, and ignite to expel Am salts, add a few crystals of pure oxalic acid and one or two drops of water, evaporate solution and again ignite ; add water and filter ; evaporate the filtrate or the main portion of the group to dryness ; if there is no residue K and Na are absent.[1] Dissolve the residue in a very little H_2O with one or two drops of HCl, and test a portion for K by $PtCl_4$ and a few drops of alcohol in a watch glass.

PRECIPITATE is yellow and crystalline, and consists of $(KCl)_2PtCl_4$. Confirm by flame coloration on Pt wire—violet. **K is present**	REMAINDER OF SOLUTION IN H_2O. Test for Na by flame coloration —golden yellow. [Na may be confirmed by filtering off the ppt. of $(KCl)_2PtCl_4$, removing excess of $PtCl_4$ (known by yellow colour of solution), by adding a grain of pure sugar, evaporating to dryness and igniting. The residue is then treated with H_2O, filtered, and the filtrate evaporated to dryness; if Na were present, there will be a residue of NaCl.] **Na is present.**

The separation depends on the insolubility of $MgAmPO_4$ for the detection of Mg, which is then removed by driving off Am salts, and converting the bases into carbonates by ignition with oxalic acid, $MgCO_3$ being insoluble in H_2O and alkaline carbonates. The K is detected by its reaction with $PtCl_4$. Na is rarely separated out, the golden flame coloration being usually relied on.

If it is desired in Group V. to detect the bases of the group without separating them, the following simpler method may be adopted :—

Evaporate the solution to dryness and ignite so as to expel

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[1] Should H_3PO_4 be present, in the absence of Mg and Groups III. and IV., it would form a residue here ; under such circumstances, therefore, a residue is no proof of the presence of K and Na. H_3PO_4 will have been tested for between Groups II. and III. ; if present, and it be desired to separate out Na, the H_3PO_4 must be removed by the addition of AmHO, ammonium acetate and dilute Fe_2Cl_6 solution as directed in Table E. The separation may then be proceeded with by adding HCl and $PtCl_4$.

Am ; if there be no residue all members of the group are absent. Dissolve the residue in H_2O and

Test a portion of the solution for **Mg** by adding AmCl, AmHO, and Na_2HPO_4.

Test a second portion for **K** by adding HCl and $PtCl_4$: confirm by flame coloration.

Test for Na by flame coloration.

The presence of H_3PO_4 does not interfere with the reactions of K and Na.

EXAMINATION FOR ACIDS.

Knowing the bases present, refer to the table of solubilities, page 392, as, if the substance were soluble in H_2O, certain acids must be absent : thus a substance soluble in H_2O or HCl and containing Ba cannot also contain H_2SO_4.

The presence or absence of **nitric, chloric, silicic,** and **phosphoric** acids will have been determined when examining for **bases.**

PRELIMINARY EXAMINATION.

TREAT A LITTLE OF THE POWDERED SUBSTANCE IN A TEST-TUBE WITH DILUTE HCl—WARM GENTLY.[1]

RESULT.	DEDUCTION. Presence of -
Colourless, odourless gas evolved, which turns lime-water milky.	CO_2 from carbonates.
A gas evolved, having the odour of rotten eggs, which blackens lead-paper.	SH_2 from certain sulphides.

[1] When told to warm gently, the heat must not be sufficiently intense to drive off fumes of the acid reagent being used.

TREAT ANOTHER PORTION OF THE POWDERED SUBSTANCE
    WITH CONCENTRATED H_2SO_4—WARM GENTLY.

RESULT.	DEDUCTION.
CO_2 and SH_2 as on treatment with HCl.	
Nitrous fumes evolved and odour of $HNO_.$[1]	**HNO_3,** also indicated by deflagration on charcoal. Confirm by adding to aqueous solution of the ‾substance mixed with H_2SO_4, $FeSO_4$.
Greenish-yellow explosive gas evolved.	Cl_2O_4 from **chlorates,** also indicated by deflagration on charcoal.
Pungent acid fumes evolved.	**HCl, HF.** Add a little MnO_2, Cl is evolved from **HCl.** The glass is corroded. Introduce into the mouth of the tube a glass rod moistened with a drop of H_2O, film of SiO_2—from **HF.** Confirm by etching on glass.
Acid fumes and reddish-brown vapours evolved, condensing into minute drops on the sides of the tube.	**HBr.**
Acid fumes and violet vapours evolved.	**HI.** Confirm by cooling the tube and then adding CS_2—violet coloration through I being dissolved.

Examination in the Wet Way.

The acids do not admit of such ready and complete classi-
fication as the bases, therefore in many instances special tests
for certain acids are absolutely necessary.

[1] In the presence of an iodide, or bromide, this reaction of HNO_3 is very
likely to be overlooked ; if there have been any indications of a nitrate given
by the preliminary examination for the bases, test specially by H_2SO_4 and
$FeSO_4$.

In preparing solutions for acids care must be taken to avoid the not uncommon error of dissolving the substance in the very acid to be tested for. For this reason separate portions of solution are prepared in different acids for the different tests.

The preliminary examination will have furnished the most characteristic tests for CO_2, **HF**, and **HNO₃** ; these and the acids detected in the examination for bases need not, therefore, be further tested for.

Test systematically for other acids as follows :—

H₂SO₄.—Treat a portion of the original substance with H_2O and a little dilute HCl; heat very gently, and filter from any insoluble residue if necessary. Test the filtrate or solution by adding $BaCl_2$, and heating—white ppt. of $BaSO_4$. **H₂SO₄ is present.**

Sulphides not decomposed by dilute HCl.—The presence of these will have been indicated by treatment with aqua regia, which liberates plastic S. The aqua regia solution also gives a H_2SO_4 reaction from the oxidation of the S. To test for these sulphides in the presence of sulphates, treat the substance with successive quantities of boiling water until these washings, after being acidulated with HCl, no longer afford a ppt. with $BaCl_2$; then treat the residue with aqua regia and test the solution for H_2SO_4 by $BaCl_2$—white ppt. of $BaSO_4$. **H₂SO₄, produced by oxidation of sulphides, is present.**

HCl, HBr, HI.—Treat a portion of the original substance with H_2O and a little dilute HNO_3, heat very gently, and filter from any insoluble residue if necessary. To the solution or filtrate add $AgNO_3$—

White curdy ppt. of AgCl sol. in AmHO. **HCl is present.** Confirmed by preliminary examination.

Pale yellow ppt. of AgBr slightly sol. in AmHO. **HBr is present.** Confirmed by preliminary examination.

Yellowish-white ppt. of AgI almost insol. in AmHO. **HI is present.** Confirmed by preliminary examination.

Separation of HCl, HBr, and HI.—Wash the pptd. silver salts with water ; heat a small portion in a test-tube with conc. H_2SO_4. AgI is decomposed by this treatment with liberation of free I, which may be recognised by its colour in the tube. AgCl and AgBr are not acted on by H_2SO_4. In this way the presence or absence of iodides is determined.

An Iodide being present.—Prepare the following reagent. Mix

together some solution of $CuSO_4$ and strong H_2SO_3, and heat gently. In this way cuprous sulphate, Cu_2SO_4, is formed. Add to the original HNO_3 solution of the substance some of this Cu_2SO_4 and warm gently, cuprous iodide, Cu_2I_2, is pptd. ; heat with this reagent until no more ppt. is formed, thus showing that the whole of the iodide has been removed. Next proceed in the following manner.

Iodides being absent.—Render the solution alkaline by adding pure KHO, and evaporate to dryness. Mix the residue with about four times its weight of powdered potassium bichromate, $K_2Cr_2O_7$, and transfer to a small retort. Add some concentrated H_2SO_4, and place the stem of the retort in a test-tube containing distilled water. (Care must be taken that no trace of the mixture gets into the stem of the retort). Heat very gently ; if bromides be present, reddish-brown vapour of bromine is liberated and is carried over into the test-tube. If chlorides be present, a volatile compound of chlorine with chromium and oxygen, termed chlorochromic acid, CrO_2Cl_2, is formed and distils over also as a reddish-brown vapour. Distil as long as any coloured vapour is evolved.

Test the water for bromine by adding CS_2 and shaking up—brown coloration of the CS_2 shows that **bromides are present.**

Decant the water from the CS_2 and add to it excess of AmHO, acetic acid in excess, and then lead acetate solution— a yellow ppt. of lead chromate shows that CrO_2Cl_2 has distilled over, and consequently that **chlorides are present.**

$HClO_3$.—This acid is in most cases sufficiently recognised in the preliminary examination ; its presence may further be confirmed by ignition of the substance and testing for HCl. If chlorides be present, first remove these by precipitation with $AgNO_3$, filter, evaporate to dryness, and ignite the residue ; dissolve in H_2O with a little HNO_3 and test by adding $AgNO_3$ —white ppt. of AgCl. **$HClO_3$ is present** in original substance.

H_3BO_3.—Mix a portion of the substance with conc. H_2SO_4 and alcohol, and set fire to the mixture. If Cu or Ba be present, perform the reaction in a flask, inflaming the vapour— green flame coloration. **H_3BO_3 is present.**

Example showing how Analytic Results should be written.

Substance given for analysis — a light grey powder.

Heated a little of the substance in a dry tube.

Result.	Deduction. Presence of—
White sublimate, dark-coloured residue.	*Am, Hg, As.* Tested specially for Am by heating a portion with NaHO—no ammoniacal odour. Am is absent. Heated another portion of the original substance with fusion mixture — liquid metallic Hg.

Heated a portion of the substance on charcoal before the blowpipe in oxidizing flame.

Dark-coloured residue.	*CuO, etc.* Heated in borax bead in O.F.—Amethyst bead. *Mn.* Tested specially for *Mn* by heating with fusion mixture and KNO_3 on Pt foil— bluish-green mass. *Mn.*

Heated a portion of the substance with fusion mixture in the reducing flame.

No special reaction.	*Zn, etc., absent.*

Heated a portion of the substance, moistened with HCl, in the Bunsen flame.

No reaction.	*Cu, etc., absent.*

Tested the solubility of the substance, first with H_2O, partly soluble ; second with dilute HCl, dissolved readily with effervescence.

2 C

	To portion of solution added HCl—			
No ppt.	*Diluted solution and passed H₂S—*			
	Black ppt. Filtered and washed.	*Boiled filtrate till free from H₂S. Tested portion for H₃PO₄—absent. Added to small portion AmCl and AmHO—no ppt. Added these reagents and H₂S to the main portion—*		
		Tawny yellow ppt. Filtered and washed.	*To filtrate added AmHO and Am₂CO₃.*	
			No ppt.	*Reserved solution for tests for Group V.*

Examination of Group II. ppt.

	Washed, transferred to a test-tube, and digested with NaHO—			
Residue.—Washed, boiled with conc. HNO₃, diluted and filtered.				*Solution—acidulated with HCl—*
Residue is black, and consists of . HgS. Confirmed by dry reaction in preliminary.	*Solution, added H₂SO₄ and alcohol—*			*No ppt.*
	No ppt.	*Boiled off alcohol and added AmHO in excess—*		*As, Sb, and Sn are absent.*
Hg is present as a mercuric salt.	*Pb is absent.*	*No ppt.*	*Solution is not blue; added SH₂ solution.*	
		Bi is absent.	*No ppt.*	*No blue coloration.*
			Cd is absent.	*Cu is absent.*

Examination of Group III. B ppt.

The ppt. being light-coloured, Ni and Co are absent; washed, added excess of NaHO, heated and filtered—	
White ppt., which rapidly turned brown	*Filtrate—added SH₂. No ppt.*
Confirmed by preliminary reactions.	*Zn is absent.*
Mn is present.	

Examination of Solution for Group V.

To a portion added Na_2HPO_4, and shook violently —	
No ppt. *Mg is absent.*	*Evaporated the main portion of the Group solution to dryness and ignited—no residue.* *K and Na are absent.*

EXAMINATION FOR ACIDS.

Added HCl to a portion of the substance in a test-tube.

Result.	*Deduction.*
Colourless, odourless gas evolved, which turned lime-water milky.	CO_2 from a carbonate.

Added conc. H_2SO_4 to another portion of the substance, and heated.

At a comparatively high temperature, a slight quantity of acid fumes evolved.	HCl. Added a little MnO_2—Cl was evolved, from HCl.

SPECIAL TESTS IN THE WET WAY.

For
H_2SO_4.—*Added $BaCl_2$ to portion of HCl solution—no ppt.*
        H_2SO_4 is absent.
HCl.—*Added H_2O and HNO_3 to portion of original sub-*
        stance, and then added $AgNO_3$—white curdy ppt.
        of AgCl, readily soluble in AmHO.   HCl is present.
H_3BO_3.—*Mixed a portion of the substance with conc. H_2SO_4*
        and alcohol, and set fire to the mixture—no green
        flame coloration. H_3BO_3 is absent.
Results of Analysis.   Found—
                Bases—HgO, MnO.
                Acids—CO_2, HCl.

DIRECTIONS FOR THE ANALYSIS OF UNKNOWN SUBSTANCES
CONTAINING ORGANIC ACIDS IN COMBINATION WITH
INORGANIC BASES.

The methods employed for the analysis of these substances
are in the main similar to those used in the case of inorganic
compounds ; somewhat greater care is, however, necessary in
discriminating between the various acids.

PRELIMINARY EXAMINATION FOR BASE.—This is to be
conducted in the same manner as with inorganic salts, except
that the reactions of the various inorganic acids given in the
table for the preliminary examination need not be looked for;
but instead the following ADDITIONAL reactions in a dry tube
may occur :—

HEAT A PORTION OF THE POWDERED SUBSTANCE IN A
DRY TUBE.

RESULT.	DEDUCTION. Presence of—
Gas evolved, which burns with a peach - blossom - coloured flame.	Cy, from certain cyanides.
Acetone is evolved.	From acetates.
Crystalline sublimate is formed, and incense-like odour evolved.	Benzoic acid.
Crystalline sublimate is formed, and fumes which cause violent coughing.	Succinic acid.
Crystalline sublimate is formed, and abundance of white fumes.	Oxalic acid.
CO is evolved.	From formates and oxalates.
Odour of burnt sugar evolved, and carbonaceous residue.	Tartaric acid.
Pungent acid fumes, and carbonaceous residue (also slight odour of burnt sugar.)	Citric acid.

In the examination for bases in the wet way, proceed as
directed in the tables as far as the separation of Group II., then,
after boiling the filtrate till free from SH, add a little conc.
HNO_3, evaporate to complete dryness, and ignite the residue,

which should be kept at a red-heat until any C present is burned away.[1] When cool, add a little conc. HCl, dissolve in H_2O, and add AmCl and AmHO ; proceed for the rest of the table as with an inorganic compound. The organic acids are destroyed at this stage of the analysis by ignition, because the presence of some of them prevents the precipitation of the members of Group III. A. Ignition is not advisable before commencing the analysis, as thereby Hg and As salts would be expelled.

EXAMINATION FOR ACIDS.

The preliminary examination must be made with very great care, as a systematic separation of the organic acids is in many instances only performed with difficulty.

PRELIMINARY EXAMINATION.

HEAT A PORTION OF THE SUBSTANCE IN A TEST-TUBE WITH CONC. H_2SO_4.

RESULT.	DEDUCTION. Presence of—
Gas evolved having odour of bitter almonds.	**HCy.** Confirm by allowing the gas to act on a drop of SAm_2 on a watch-glass, and subsequently testing by Fe_2Cl_6 (see page 362).
Odour of formic acid	**Formic acid.**
Smell of vinegar	**Acetic Acid.** Confirm by adding single drop of alcohol and observing smell of acetic ether.
CO and CO_2 evolved (gases which respectively are inflammable, and turn lime-water milky).	**Oxalic acid.**
CO, CO_2 and SO_2 evolved with blackening of the mixture.	**Tartaric acid.**
CO and CO_2 evolved, but mixture does not blacken until after some time, when SO_2 is also evolved.	**Citric acid.**

[1] In the absence of a ppt. with HCl and SH_2, time may be saved by igniting a portion of the original substance instead of evaporating to dryness.

The preliminary tests for organic acids depend largely on the sense of smell ; the reactions should therefore be carefully made on the known substances until the various odours can be recognised with certainty.   When more than one acid is present the difficulty is increased, but even then the different acids may often be detected.   Apply to the nose several times during the experiment, as the reactions of the whole of the acids do not occur at the same temperature, and thus they may frequently be detected in succession.   Many persons are unable to smell HCy ; when such is the case, special tests must be made for the detection of that acid.

SEPARATION IN THE WET WAY.

If sulphuric acid give a reaction in the preliminary examination, introduce a portion of the substance in a small retort, add dilute H_2SO_4, and distil : acetic and formic acids, if present, will be found in the distillate ; to a portion of this add $Hg_2(NO_3)_2$ and beat gently—grey ppt. of metallic Hg.   **Formic acid is present.**

To test for the remaining acids, prepare a solution in the following manner :—If the metals of Groups I. and II. be present, remove them by their respective group reagents, boil off SH_2, and filter ; add slight excess of Na_2CO_3 to filtrate, and boil for five minutes, filter off any ppt. and test filtrate for acids.   In the absence of Groups I. and II. proceed at once to adding Na_2CO_3 ; if the only bases present are Na_2O and K_2O, the subsequent tests may be made directly on the original solution.

Acidulate a portion of the solution thus prepared by HNO_3, add $AgNO_3$ in slight excess : a white ppt. is formed consisting of AgCl (from the HCl used in separating Group I.), and AgCy if HCy be present.   Wash, dry and ignite the ppt. : AgCy, if present, is decomposed with separation of metallic Ag (AgCl remains unaltered).   Dissolve in HNO_3, filter, and add HCl— white ppt. of AgCl.   **HCy is present in substance.**

In the known absence of HCl, the ppt. with $AgNO_3$ can only be AgCy.   Care must be taken that in igniting the ppt. no reducing action takes place—thus none of the filter must be present.

Neutralise the main portion of the solution if alkaline (from the addition of Na_2CO_3) by adding dilute HNO_3 drop by drop,

and boiling, until a slightly acid reaction is obtained on testing with litmus ; then exactly neutralise by adding a drop (or two) of dilute NaHO. Neutralise if acid (from original substance containing a free organic acid), by adding NaHO drop by drop until without action on litmus-paper.

Table for the separation of Organic Acids.

To the neutral solution add large excess of CaCl₂, shake up, allow to stand for twenty minutes, and filter.				
PRECIPITATE.—Wash, add cold NaHO, and filter.		FILTRATE.—Boil for some minutes.		
RESIDUE consists of calcium oxalate. Confirm by gentle ignition, CaCO₃ is produced and effervescence on addition of HCl. **Oxalic acid is present.**	SOLUTION.—Boil, calcium tartrate, if present, is reppted. Confirmed by reactions in preliminary examination. **Tartaric acid is present.**	PRECIPITATE consists of calcium citrate. Confirm by dissolving in HCl and re-ppting. by AmHO ; also by preliminary reactions. **Citric acid is present.**	FILTRATE.—Add three times the volume of alcohol, and filter.	
			PRECIPITATE consists of calcium succinate. Confirmed by reaction when heated in dry tube. **Succinic acid is present.**	FILTRATE.—Boil off alcohol ; add neutral solution of Fe₂Cl₆—pale yellow ppt. **Benzoic acid is present.**

It is necessary before testing for the organic acids to remove the heavy metals, as they interfere with certain of the reactions ; ammonia, if present, is also expelled (by boiling with Na₂CO₃) for the same reason.

The NaHO, used for the separation of oxalic and tartaric acids, must be free from carbonate. To effect this, add some lime to the NaHO solution, shake up, allow to subside, and draw off the clear solution, as wanted, with a small pipette. Keep the bottle closely stoppered and shake up from time to time.

The Fe₂Cl₆ used for the precipitation of ferric benzoate must contain no free acid ; to effect this, add a drop of AmHO, so as to produce a slight ppt., and filter. The separation of the organic acids must throughout be conducted with great care.

I. TABLE OF SOLUBILITIES.—(See Page 381.)

(Thorpe and Muir.)

This table is so arranged that the *bases* are placed at the heads of the columns, the *acids* with which they may be combined at the side.

The figures refer to the various *menstrua* in which the salts are soluble.   Thus :

> I.   means soluble in water.
> II.   means soluble in acids, but insoluble in water.
> III. means insoluble in both water and acids.

The solubilities of the more commonly occurring salts are indicated by large letters I. II. III., while those which are of less frequent occurrence have small letters placed after them— 1, 2, or 3.

Some substances belong to more than one class—this is indicated thus : 1-2 means a substance difficultly soluble in water, but soluble in acids.   1-3 means a substance soluble with difficulty in water, the solubility of which is not increased by the addition of acids.

2-3 means a substance insoluble in water, and but slightly soluble in acids.   The solubilities of the more commonly occurring double salts are given in a separate table.   In this table a few of the simple and compound Cyanides are also enumerated.

A small number attached to the figure indicating the solubility of a substance, thus II$_r$, means that further information is given in the notes to the table.

Bases.

Acids and Halogens, &c.	Group I.			Group II. Div. 1				Group II. Div. 2 — See Acids				
	PbO II.	Ag_2O 2	Hg_2O II.	HgO II.	Bi_2O_3 2	CuO II.$_2$	CdO 2	As_2O_5 I.-II.	As_2O_5 II.	SnO 2	SnO_2 2-3	Sb_2O_3 2
S	2 I.-III.	2$_3$ III.	II.$_1$ II.-III.	II.$_4$ I.	2 I.	2 I.	2 I.	II.$_3$	II.$_3$	2$_6$ I.	2$_6$	2$_7$ I.
Cl	II.	III.	II.	I.	I.	I.	I.			2	—	
I	II.-III.	I.-III.	1-2		—		—			—	—	
SO_3	I.	I	I.	I.	I.	I.	I.					
NO_3	2	2	2	I.	L$_3$	I.	I.					
PO_4	II.	—	2	2	2	2	2					
CO_3	2	2		2	2	2	2				2	1-2
BO_3	II.	2	2	2		—	1-2				2	2
C_2O_4	—	2	2	2	2	2	2					2
ClO_3	2	2	1-2	—		II.	—					1
As_2O_3	2	—	2	2	2	I.^{II}				1-2		I.
As_2O_5	I.	2	1-2	2		1	—			2	—	
$C_2H_3O_2$	2	—	1-2	—	2	—	1-2					
$C_4H_4O_6$	—	1	1	2	—	—	—					
CHO_2	2	2	2			—	—					

Bases (continued).

Acids and Halogens, &c.	Group III.				Group IV.				Group V.				Group VI.		
	FeO II.	Fe₂O₃ II.	Cr₂O₃ II.-III.	Al₂O₃ II.	CoO II.ₐ	NiO II.ₐ	ZnO II.	MnO II.	BaO I.	SrO I.	CaO I.-II.	MgO II.	(NH₄)₂O I.	Na₂O I.	K₂O I.
S . . .	II.	II.			II.ₐ	II.ₐ	II.	II.	I.	I.	I.-II.	2	I.	I.	I.
Cl . . .	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.
I . . .	I.	I.		I.		I.	I.	I.	I.	I.	I.	I.	I.	I.	I.
SO₄ . . .	I.	I.	I.	I.	I.	I.	I.	I.	III.	III.	I.-III.	I.	I.	I.	I.
NO₃ . . .	I.	II.	I.	I.	2	2	I.	I.	I.	I.	I.	I.	I.	I.	I.
PO₄ . . .	2		2	2	2	2	2	2	2	2	II.	2	I.	I.	I.
CO₂ . . .	2	2		2	2	2	2	2	2	2	II.	2	I.	I.	I.
BO₃ . . .	2	I.		I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.
C₂O₄ . . .	I-2	2	I.	I.	2	2	3	2	2	2	2	2	I.	I.	I.
ClO₃ . . .	I.	2	I.	I.	2	2			2	I.	I.		I.	I.	I.
As₂O₃ . . .	2	I.		I.	2	2	2		L.	I.	II.	I-2	I.	I.	I.
As₂O₅ . . .	2	I.	I.	2	I.	I.	I.		2	I.	I.		I.	I.	I.
C₂H₃O₂ . . .	I-2	I.		I-2	I-2	I.	I.	I-2	L.	2	II.	I-2	I.	I.	I.
C₄H₄O₆ . . .	I.	I.		I-2		2	2	I.	2	I.	2	I.	I.	I.	I.
CHO₂ . . .	I.	I.			I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.
C₆H₅O₇ . . .	I.	I.	I.			2	2	I.	2	I.	2	I.	I.	I.	I.

TABLE OF SOLUBILITIES.—No. 2.

Cyanide of Potassium	I.
Ferrocyanide ,, ...	I.
Ferricyanide ,, ...	I.
Ferrocyanide of Zinc and Potassium	II.
Prussian blue	III.

DOUBLE SALTS.

Potassium-aluminium sulphate	I.
Aluminium-ammonium sulphate	I.
Potassium-ammonium tartrate	I.
,, *Sodium* ,, ...	I.
,, *Ferric* ,, ...	I.
,, *Antimony* ,, ...	I.
Sodium-ammonium phosphate	I.
Ammonium-copper chloride	I.
,, *Mercury* ,, ...	II.
Platinum-ammonium ,, ...	1–3.
,, *Potassium* ,, ...	1–3.

NOTES TO TABLE OF SOLUBILITIES.

1. *Hydrochloric acid* converts *minium* into chloride insoluble in excess of the reagent. Nitric acid dissolves it partially, but converts some of it into insoluble brown lead peroxide.

2. *Antimonious oxide*, soluble in hydrochloric, but insoluble in nitric acid.

3. *Silver sulphide*, soluble only in nitric acid.

4. *Mercurous and mercuric sulphides*, soluble only in aqua regia.

5. *Arsenic sulphides*, decomposed slightly by boiling strong hydrochloric acid, but decomposed and dissolved by nitric acid.

6. *Tin sulphides* are decomposed and dissolved by hydrochloric acid, nitric acid converts them into insoluble hydrates.

7. *Antimonious sulphide*, dissolves in strong hydrochloric acid.

8. *Nickel and cobalt sulphides*, much more easily decomposed and dissolved by nitric than by hydrochloric acid.

9. *Basic bismuth nitrate*, soluble in acids.

10. *Basic lead acetate*, partially soluble in water, completely so in acids.

LIST OF REAGENTS.

Sodium Hydrate, NaHO. Dissolve one part of the pure sticks or lumps in ten parts of water.

Sodium Phosphate, Na₂HPO₄. One part to ten of water.

Sodium Carbonate, Na₂CO₃. One part to five of water.

Potassium Ferrocyanide, K₄FeCy₆. One part to twelve of water.

Potassium Cyanide, KCy. One part to eight of water. (Solution made only when required.)

Ammonium Oxalate, Am₂C₂O₄. One part to twenty-four of water.

Ammonium Chloride, AmCl. One part to six of water.

Ammonium Carbonate, Am₄CO₃. One part to five of water, and one part of strong ammonia.

Ammonium Sulphide, Am₂S. Three parts of concentrated hydric ammonic sulphide, two of strong ammonia, and fifty of water.

Ammonium Hydrate, AmHO. One part of concentrated solution to three of water.

Ammonium Sulphate, Am₂SO₄. Make a saturated solution.

Barium Chloride, BaCl₂. One part to ten of water.

Ferric Chloride, Fe₂Cl₆. One part to ten of water.

Calcium Chloride, CaCl₂. One part to five of water.

Silver Nitrate, AgNO₃. One part to twenty of water.

Lead Acetate, Pb(C₂H₃O₂)₂. One part to ten of water.

Cobalt Nitrate, Co(NO₃)₂. One part to ten of water.

Acetic Acid, HC₂H₃O₂. One part of the glacial acid to two of water.

Sulphuric Acid (dilute), H₂SO₄. One part of the concentrated acid to five of water.

Nitric Acid (dilute), HNO₃. One part of the concentrated acid to three of water.

Hydrochloric Acid (dilute), HCl. One part of the concentrated acid to three of water.

Sulphuretted Hydrogen solution, H₂S. Pass the washed gas into water until saturated.

Borax.
Fusion Mixture. } Used in the solid state

LIST OF REAGENTS.

Sodium Hydrate, $NaHO$. Dissolve one part of the pure sticks or lumps in ten parts of water.

Sodium Phosphate, Na_2HPO_4. One part to ten of water.

Sodium Carbonate, Na_2CO_3. One part to five of water.

Potassium Ferrocyanide, K_4FeCy_6. One part to twelve of water.

Potassium Cyanide, KCy. One part to eight of water. (Solution made only when required.)

Ammonium Oxalate, $Am_2C_2O_4$. One part to twenty-four of water.

Ammonium Chloride, $AmCl$. One part to six of water.

Ammonium Carbonate, Am_4CO_3. One part to five of water, and one part of strong ammonia.

Ammonium Sulphide, Am_2S. Three parts of concentrated hydric ammonic sulphide, two of strong ammonia, and fifty of water.

Ammonium Hydrate, $AmHO$. One part of concentrated solution to three of water.

Ammonium Sulphate, Am_2SO_4. Make a saturated solution.

Barium Chloride, $BaCl_2$. One part to ten of water.

Ferric Chloride, Fe_2Cl_6. One part to ten of water.

Calcium Chloride, $CaCl_2$. One part to five of water.

Silver Nitrate, $AgNO_3$. One part to twenty of water.

Lead Acetate, $Pb(C_2H_3O_2)_2$. One part to ten of water.

Cobalt Nitrate, $Co(NO_3)_2$. One part to ten of water.

Acetic Acid, $HC_2H_3O_2$. One part of the glacial acid to two of water.

Sulphuric Acid (dilute), H_2SO_4. One part of the concentrated acid to five of water.

Nitric Acid (dilute), HNO_3. One part of the concentrated acid to three of water.

Hydrochloric Acid (dilute), HCl. One part of the concentrated acid to three of water.

Sulphuretted Hydrogen solution, H_2S. Pass the washed gas into water until saturated.

Borax.
Fusion Mixture. } Used in the solid state

Sodium Hypochlorite, NaClO. Dissolve six parts of bleaching powder ($CaOCl_2$) in seven parts of water; add twelve parts of crystallised sodium carbonate, dissolved in the smallest possible quantity of water: shake up, allow to subside, and filter off the clear liquid, which is a solution of $NaClO$.

Potassium Ferricyanide, $K_6Fe_2Cy_{12}$. One part to twelve of water. (Solution made only when required.)

Potassium Chromate, K_2CrO_4. One part to eight of water.

Potassium Iodide, KI. One part to twenty of water.

Potassium Nitrate, KNO_3. Used in the solid state.

Ammonium Sulphocyanide, AmCyS. One part to ten of water.

Ammonium Acetate, $AmC_2H_3O_2$. One of concentrated solution to one of water.

Ammonium Molybdate, Am_2MoO_4. Dissolve 150 grammes of the salt in one litre of water, and pour into one litre of dilute nitric acid (one of acid to one of water). The acid must not be poured into the solution cf the salt.

Mercuric Chloride, $HgCl_2$. One part to sixteen of water.

Platinum Chloride, $PtCl_4$. One part to ten of water.

Magnesium Sulphate, $MgSO_4$. One part to ten of water.

Stannous Chloride, $SnCl_2$. Dissolve by boiling with a little concentrated hydrochloric acid; to one part of the salt add four parts of water. Keep some granulated tin in the bottle.

Calcic Sulphate, $CaSO_4$. Shake up the salt with water, and decant the saturated solution.

Ferrous Sulphate, $FeSO_4$. One part to ten of water. (Solution made only when required.)

Tartaric Acid, $H_2C_4H_4O_6$. One part to three of water. (Solution made only when required.)

Concentrated Sulphuric, Nitric, and Hydrochloric Acids.

Sulphurous Acid Solution, H_2SO_3. Pass the washed gas into water until saturated.

Lime Water, $Ca(HO)_2$. Place some quicklime into a bottle, add water, shake up, allow to subside, and decant the clear solution.

Barium Hydrate, $Ba(HO)_2$. One part to twenty of water, shake up, allow to subside, and decant the clear solution.

Hydrogen Potassium Sulphate, $KHSO_4$. Used in solid state.

Starch. Shake up one of starch to about twenty of cold water, boil, and allow to cool. (Solution made only when required.)

Microcosmic Salt, $NaHAmPO_4$. Used in solid state.

Methylated Spirit. Use the commercial spirit.

Alcohol. Use the '*Sp. Vini. Rect.*' of the chemist.

QUESTIONS AND EXERCISES

WITH which are incorporated the whole of the Inorganic Chemistry questions set during the years 1886-92 inclusive, both by the Science and Art Department in the Elementary Stage, and the London University in the Matriculation Examination.

The questions are arranged, so far as practicable, in the order of the text.

1. Define ' chemistry,' ' element,' ' compound,' ' mixture.'

2. Describe any experiments you have witnessed which serve to illustrate the difference between mixture and chemical combination.

N.B.—You are desired not to attempt the description of experiments which you have not seen.

London University Matriculation, 1892.

3. Describe an experiment you have actually seen performed which affords an example of chemical action.

Science and Art, 1890.

4. Describe an experiment to illustrate the indestructibility of matter in the case of a burning candle. Give a drawing of the apparatus you would use. *S. and A.,* 1878.

5. It is stated that matter is indestructible ; describe any experiments which confirm the truth of this statement.

S. and A., 1881.

6. In what ways do a mixture of copper and sulphur differ after being heated from their condition previous to the application of heat ?

7. Describe the relation which exists between chemical action and other forces, especially *heat*.

8. Explain the meaning of the terms 'analysis' and 'synthesis,' and give two cases of each in illustration.

S. and A., 1886.

9. How can you show that the volume of a gas is changed by temperature and pressure ?

S. and A., 1890.

10. What are the effects respectively of 'gravitation,' 'cohesion,' and 'chemical action' on matter ?

11. In what way does chemical attraction differ from the other natural forces ? Mention some experiments which illustrate this difference.

12. A wooden lath is suspended horizontally by means of a thread. A dry glass rod or tube is now briskly rubbed with warm silk, and then brought near to one end of the suspended lath : what occurs? *S. and A.,* 1876.

13. What happens when a glass rod moistened with concentrated sulphuric acid is brought very near to a small heap of a mixture of sugar and potassic chlorate, but so as not to touch the heap ? *S. and A.,* 1876.

14. Mention and describe the different modes of chemical action. Give at least one experimental illustration of each.

15. What takes place when solution of mercuric chloride is added to solution of potassic iodide ? *S. and A.,* 1875.

16. A white powder is shaken up with distilled water : how would you ascertain whether any of it dissolves ?

S. and A ., Pract., 1880.

17. A glassful of dirty water is given to you. Describe with sketch the plan you would adopt, first, for rendering the water clear, and secondly, for ascertaining whether the clear water contains any dissolved solid matter.

S. and A., 1880.

18. How would you prepare pure water and common salt from sea-water ? *L. U. M.,* 1892.

19. Explain the meaning of the terms 'sublimation,' 'volatile,' 'fixed,' and 'ignition.'

20. Give a short account of the metric system of weights and measures.

21. Express in English weights and measures 500 grams, 500 cubic centimetres, 500 millimetres.

Find the weight in grams of 350 c.c. of sulphuric acid of density 1·8. *S. and A.,* 1891.

22. Define the gram and the litre. How many grams are contained in 1·725 kilogram ?

Find the weight of a block of sulphur 50 c.c. in volume and of relative density 2·05. *S. and A.*, 1892.

23. What do you understand by the *temperature* of a body, and how is it measured?

24. Describe the Fahrenheit and Centigrade scales. Convert 200° and − 10° C. into Fahrenheit, and 60° and −40° F. into Centigrade degrees.

$$\frac{200° \text{ C.} \times 9}{5} + 32 = 360 + 32 = 392° \text{ F.}$$

$$\frac{(60° \text{ F.} - 32) \times 5}{9} = \frac{28 \times 5}{9} = 15·5° \text{ C.}$$

25. Define *quantity of heat,* and explain wherein it differs from temperature.

26. What is meant by *absolute temperature?* State the laws governing the relation of the volume of a gas to its pressure and temperature.

27. Classify the chief elementary substances into metals and non-metals, and into positive and negative elements.

S. and A., 1875.

28. By what properties is a metal distinguished from a non-metal? Arrange the following elements under the above heads : Cl, K, P, S, N, Na, As, H, Fe. *S. and A.*, 1879.

29. Mention the elements which at ordinary temperatures are respectively gases and liquids. State the approximate composition of the earth's crust.

30. Explain carefully what is meant by 'symbol,' 'formula,' and 'chemical equation.'

31. What is understood by the terms 'atom,' 'combining proportion,' 'combining weight,' and 'atomic weight'?

32. Explain the meaning in chemistry of the word 'molecule.' Write in words the meaning of each of the following symbols : H, O, O_2, O_3, $3H_2$, NH_3. *L. U. M.*, 1891.

33. What do you understand by the density of a gas? The volume of a given weight of a gas has to be calculated at the standard temperature and pressure : what does this mean?

S. and A., 1888.

34. Give an account of the discovery of oxygen.

35. You have given to you some *red precipitate* (mercuric oxide) : state (1) whether you consider this substance to be a

2 D

simple or a compound body; (2) whether it undergoes any chemical change when submitted to the action of heat ; and if so, (3) what is the nature of the change, and how it can be expressed symbolically.   *S. and A.*, 1874.

36. How would you prove by experiment that mercuric oxide is a compound and not an elementary substance? Sketch and describe the apparatus you would use for this purpose.
                                                    S. and A., 1880.

37. I heat potassic chlorate in a flask until effervescence commences : what chemical change takes place? I then drop into the flask some peroxide of manganese : what happens?
                                                    S. and A., 1879.

38. What are the resulting products when hydrogen, carbon, sulphur, and phosphorus are burnt in oxygen? Express the reactions by equations.   *S. and A.*, 1874.

39. I heat, as strongly as possible, a fragment of each of the following substances in a glass tube through which a current of air is passing : sulphur, phosphorus, charcoal. What chemical changes take place?   *S. and A.*, 1876.

40. What are the principal properties of oxygen ?

41. Why does a candle burn more brightly in oxygen than in air ?   *S. and A.*, 1892.

Nitrogen, with which oxygen is mixed in air, is a very inert gas, which does not support combustion.

42. What takes place when electric sparks are passed through dry oxygen ?   *S. and A.*, 1877.

43. Some moist phosphorus is placed in a jar filled with atmospheric air, and a slip of paper which has been dipped into water containing starch and potassic iodide is suspended in the jar : state what occurs.   *S. and A.*, 1875.

44. What do you understand by an allotropic form of oxygen ? How is this substance distinguished from ordinary oxygen?   *S. and A.*, 1881.

45. What is meant by the term ' allotropic modification '? Give examples of some allotropic modifications of non-metallic elements.   *S. and A.*, 1890.

46. Describe two methods of obtaining hydrogen from water. What weight of hydrogen is contained in 250 grams of water ?   *S. and A.*, 1890.

The molecule of water, H_2O, weighs 18, and consists of 2 atoms of hydrogen, together weighing 2, and 1 atom of oxygen, weighing 16. The 250 grams contain hydrogen in the same proportion.

47. Sketch the apparatus you have seen used for preparing hydrogen (1) by the action of sodium on water, (2) by that of zinc on sulphuric acid.   *S. and A., Pract.*, 1881.

48. Translate into words the following equation :—

$$2OH_2 + K_2 = 2OKH + H_2. \quad \textit{S. and A.,} \ 1879.$$
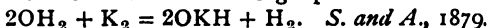
The reaction is similar to that with Na.

49. Into a boiling solution of caustic soda I drop some fragments of granulated zinc : what chemical change, if any, takes place ?   *S. and A.*, 1876.

50. Describe the chemical change which takes place when steam is passed over red-hot iron filings.

51. Describe exactly how you would show the formation of water from burning hydrogen, and sketch the apparatus.
                    S. and A., Pract., 1880.

52. What are the principal properties of hydrogen ?

53. Describe the process of gaseous diffusion, and state the law governing its rate.

54. Give examples of oxidising and reducing agents.

55. Wherein does nascent hydrogen differ in its chemical behaviour from that element in its free state ?

56. How would you prove the presence of solid and gaseous impurities in water ?

57. By what simple experiments could you distinguish three samples of water, one of which may be rain-water, another water from a well, and the third sea-water? How may the presence of air dissolved in water be demonstrated ?
                    L. U. M., 1891.

On evaporation on platinum foil, rain-water would leave practically no residue, with well-water the residue would be perceptible, while sea-water would leave a considerable mass of saline matter.

58. Describe some of the most characteristic physical and chemical properties of water, and state exactly how you would demonstrate them without the use of very special or elaborate apparatus.   *L. U. M.*, 1890.

59. Describe carefully the changes produced by raising the temperature of a piece of ice from − 10° to 150° C.

60. Explain the terms 'crystal,' 'dimorphous,' 'amorphous,' and 'water of crystallisation.'

61. Describe an experiment for proving that water is a compound body, and state precisely the conclusions to which the experiment leads you.   *S. and A.*, 1877.

62. A mixture of five volumes of hydrogen and three volumes of oxygen are exploded by an electric spark : will any gas remain ?   If so, how much, and how will you ascertain what it is ?   *S. and A.*, 1879.

63. Describe an experiment by means of which you would prove the relation which exists between the volume of hydrogen and oxygen, and of the steam produced by their combination.

64. What is the composition of water by weight, and how may it be experimentally determined ?

65. Describe two processes for the preparation of chlorine. Give an equation and a sketch of the apparatus in each case.
    S. and A., 1878.

66. By what experiments could you prove that chlorine is a constituent of (1) common salt, and (2) potassium chlorate ?
    S. and A., 1891.

This is demonstrated in the case of common salt, NaCl, by its being evolved from that body by the action of manganese dioxide and sulphuric acid.   The student already knows that potassium chlorate, $KClO_3$, is reduced to the chloride, KCl, by heat.   The chlorate of potassium can be made to yield chlorine by the similar reaction to that with sodium chloride.

67. Three pint bottles of chlorine are given to you : describe the experiments you would make with them in order to show clearly the characteristic properties of this body.
    S. and A., 1880.

68. Hydrogen burns in chlorine : how would you make this experiment ?   Give a sketch.   *S. and A.*, *Pract.*, 1881.

69. Chlorine water exposed to light loses its colour : how do you account for this ?

70. What happens when steam is passed through a red-hot porcelain tube, and when a mixture of steam and chlorine is passed through the same tube ?   *S. and A.*, 1877.

71. How does chlorine act as a bleaching agent ?   How is it prepared from salt, and what are its properties ?
    S. and A., 1890.

72. Name the materials and sketch the apparatus required for the production of dry hydrochloric acid. Explain by means of an equation the chemical change in which the acid is produced. *L. U. M.,* 1888.

73. How would you prepare pure and dry hydrogen chloride, and prove by experiment that it contains half its volume of hydrogen and half its volume of chlorine? *S. and A.,* 1891.

74. Describe the apparatus you would use, and the precise manner in which you would set to work, to prepare from common salt such a solution as is sold under the names 'spirit of salt,' 'muriatic acid,' or 'hydrochloric acid.'

L. U. M., 1891.

75. What are the principal properties of hydrochloric acid?

76. How could you prove that chlorine is a constituent of common salt and of hydrochloric acid? Calculate the percentage composition of these two substances.

S. and A., 1888.

77. Describe fully experiments showing (1) the analysis of hydrochloric acid, and (2) the synthesis of hydrochloric acid.

S. and A., 1889.

78. Describe the methods you would employ to verify the facts implied by the formula HCl. *L. U. M.,* 1886.

79. Three bottles are given you : in one is hydrochloric acid gas, in another chlorine, and in the third is ozone : by what properties and experiments would you recognise and identify each gas? *S. and A.,* 1886.

80. Describe clearly why the formula H_2O has been given to water.

81. Describe and explain any two simple experiments which serve to illustrate the law of definite proportions.

L. U. M., 1888.

82. What do you understand by the term 'chemical action'? Explain how the recognition of the fact that chemical action always takes place between definite proportions of matter led to the establishment of Dalton's atomic theory.

S. and A., 1892.

83. Calculate the percentage composition of potassium chlorate (chlorate of potash). (K = 39 ; Cl = 35·37 ; O = 16.)

S. and A., 1878.

84. What weight of oxygen gas could be obtained by the

complete decomposition of 100 grams of pure potassium chlorate? If the chlorate used contained 10 per cent. of its weight of potassium chloride, what would be the difference in the amount of oxygen obtained?   *S. and A.*, 1891.

As potassium chloride yields no oxygen, the second part of this question resolves itself into a calculation of the difference in the amount of oxygen obtained from 90 grams of chlorate as compared with 100 grams of that salt.

85. What is the percentage composition of water?
      S. and A., 1875.

The formula of water is H_2O; the molecular weight $= 2 + 16 = 18$.
Therefore 18 parts of water contain 2 parts of H.
   „   „   „   16   „   O.
As $18 : 100 :: 2 : 11\cdot11$ per cent. of H.
„ $18 : 100 :: 16 : 88\cdot88$ „.   O.

86. What is the percentage composition of hydrochloric acid?   *S. and A.*, 1874.

87. Calculate the percentages of carbon, hydrogen, and oxygen in a compound of the formula $C_{12}H_{22}O_{11}$. ($C = 12$; $O = 16$.)   *L. U. M.*, 1890.

88. Determine the percentage composition of the following substances: potassium nitrate, sulphuric acid, zinc sulphate, and ammonium nitrate.

89. What is the chemical formula of a body having the following percentage composition?—

S	.	.	.	32·65
O	.	.	.	65·31
H	.	.	.	2·04

100·00
S. and A., 1876.

Dividing each number by the atomic weight of the element—

$$\frac{32\cdot65}{32} = 1\cdot02 \text{ of S.}$$

$$\frac{65\cdot31}{16} = 4\cdot08 \text{ of O.}$$

$$\frac{2\cdot04}{1} = 2\cdot04 \text{ of H.}$$

Determining the lowest series of whole numbers having the same ratio—

$$\frac{1 \cdot 02}{1 \cdot 02} = 1 \text{ of S}; \frac{4 \cdot 08}{1 \cdot 02} = 4 \text{ of O}; \frac{2 \cdot 04}{2 \cdot 04} = 2 \text{ of H.}$$

The formula is H_2SO_4.

90. A body on analysis gave the following results : what is its formula ?—

C	.	.	.	14·29
O	.	.	.	57·14
H	.	.	.	1·19
Na.	.	.	.	27·38
				100·00

91. Calculate the formula for a body which has the following percentage composition : oxygen, 38·1 ; hydrogen, 0·8 ; phosphorus, 24·6 ; sodium, 36·5.

92. Air contains 23 per cent. of its weight of oxygen : how many grams of phosphorus are needed to burn out the whole of the oxygen in 100 grams of air when the highest oxide of phosphorus is formed? (P = 31.) *S. and A.*, 1878.

From the question, there are 23 grams of O in 100 grams of air. The chemical action when P burns in O is represented in the following equation— :

$$2P \quad + \quad 5O \quad = \quad P_2O_5$$
$$31 \times 2 = 62 \quad 16 \times 5 = 80 \quad 62 + 80 = 142.$$
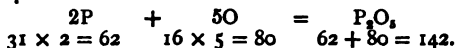
To burn out 80 by weight of O, 62 of P are required ; then—

As 80 : 23 :: 62 : 17·8 grams of P required to burn out 23 grams of O.

93. If 112 litres of hydrogen weigh 10 grams, what is the weight in grams of the same volume of chlorine, and of the same volume of hydrochloric acid gas? *S. and A.*, 1880.

The density of every gas is half its molecular weight ; the densities, therefore, of hydrogen, chlorine, and hydrochloric acid are—

$$\text{Hydrogen } \frac{2}{2} = 1$$

$$\text{Chlorine } \frac{71}{2} = 35·5$$

$$\text{Hydrochloric acid } \frac{36·5}{2} = 18·25$$

The weight of 112 litres of chlorine is therefore—

$$10 \text{ grams} \times 35·5 = 355 \text{ grams};$$

and of hydrochloric acid, 10 × 18·25 = 182·5 grams.

94. How many grams of oxygen and how many of hydrogen are required in order to prepare 500 grams of water? How many litres will the hydrogen measure if each gram measures 11·2 litres? How many litres will the oxygen measure, its density being 16 times as great as that of hydrogen?

$$H_2 + O = \underbrace{H_2O}$$
$$\quad 2 \quad\quad 16 \quad\quad 18$$
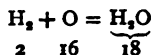
As 18 : 500 :: 2 : 55·55 grams of hydrogen.
As 18 : 500 :: 16 : 444·44 grams of oxygen.
55·55 × 11·2 = 622·16 litres of hydrogen.
$$\frac{444·44 \times 11·2}{16} = 311·10 \text{ litres of oxygen.}$$

Note.—The volume of oxygen is here calculated from the data given in the question, but the simpler and more natural method is to determine it direct from that of hydrogen. A molecular equation shows that two volumes of hydrogen unite with one of oxygen to form water; consequently, the volume of oxygen must be half that of hydrogen—

$$\frac{622·16}{2} = 311·08 \text{ litres of oxygen.}$$

Having determined the actual volume of any one gas taking part in any chemical change, the relative volumes of any others should be deduced from the molecular equation. (The slight discrepancy between the two results, as shown above, is due to decimals not being absolutely exact fractions.)

95. Hydrogen is passed over red-hot copper oxide (CuO) : how much metallic copper is produced in forming 9 grams of water, and what is the volume of hydrogen at normal temperature and pressure which has been used?   *S. and A.*, 1886.

96. Ten grams of hydrochloric acid (HCl) act on zinc, and the same weight acts on calcium carbonate : what bulk of gas, measured at the normal temperature and pressure, is produced in each case?

The following equations represent the chemical changes :—
$$2HCl + Zn = \underbrace{ZnCl_2} + \underbrace{H_2}.$$
$$\quad 73 \quad\quad 65 \quad\quad 136 \quad\quad 2$$
$$\underbrace{2HCl} + \underbrace{CaCO_3} = \underbrace{CaCl_2} + \underbrace{H_2O} + \underbrace{CO_2}.$$
$$\quad 73 \quad\quad 100 \quad\quad 111 \quad\quad 18 \quad\quad 44$$
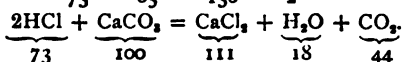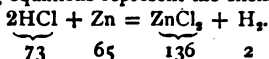
As 73 : 10   :: 2 : 0·274 gram of hydrogen evolved.
As 1 : 0·274 :: 11·2 : 3·068 litres of hydrogen evolved.

An inspection of the equations shows that two molecules of hydrochloric acid cause respectively the evolution of one molecule of hydrogen (H_2), and one molecule of carbon dioxide (CO_2) ; the volume of

the two gases must consequently be the same, and 3·068 litres of carbon dioxide are evolved.

97. How many litres of oxygen gas measured at 10° C. and 755 mm. can be obtained from 1 kilogram of potassium chlorate? (1 litre of oxygen at 0° and 760 mm. = 1·43 gram.)

S. and A., 1887.

98. What weight of oxygen is required to burn 16 grams of hydrogen to water, and what bulk of steam at standard temperature and pressure would this amount of water produce?

S. and A., 1889.

99. How many cubic centimetres of oxygen and of hydrogen are obtainable from 10 grams of water? *S. and A.*, 1888.

100. Calculate the volume of chlorine gas, measured at 10° C. and 760 mm., obtainable by heating 1 gram of pure MnO_2 with excess of hydrochloric acid. (Mn = 55 ; O = 16 ; Cl = 35·5.) *L. U. M.*, 1888.

101. Explain what is meant by the terms, ' combining proportion by weight and by volume.' Give examples.

L. U. M., 1887.

102. Write out the various names by which the following compounds are known : Fe_2O_3, CuO, Cu_2O, BaO, Fe_3O_4, NaHO, SO_3, SO_2, H_2SO_4, H_2SO_3, Na_2SO_3, K_2SO_4, $KHSO_4$.

103. What are the characteristic properties of an acid and of a base? Explain the effect of mixing sulphuric acid and caustic soda. *S. and A.*, 1881.

104. Name and give the formula of a salt, and describe how you would prepare it. *S. and A.*, 1888.

105. You are required to neutralise two quantities of 50 grams each of sulphuric acid diluted with water, the one with caustic soda, the other with sodium carbonate : describe how you would do this, and how you would ascertain that neutralisation had been effected. What difference would be noticeable between the two operations, and what quantity of product would be obtained in each case? (Na = 23.) *L. U. M.*, 1892.

The chemical actions are represented by the two following equations :—

$$H_2SO_4 \quad + \quad 2NaHO \quad = \quad Na_2SO_4 \quad + \quad 2H_2O.$$
Sulphuric acid.   Sodium hydrate   Sodium sulphate.   Water.
(Caustic soda).

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O.$$

Sulphuric   Sodium   Sodium   Carbon   Water.
acid.   carbonate.   sulphate.   dioxide.
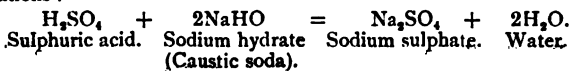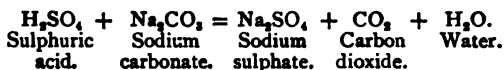
For a description of the second reaction, the student is referred to the chapter on the oxides of carbon.

The dilute acid should have a drop of litmus solution added, and then the caustic soda added either in the solid state or preferably in solution, until the red tint of the litmus changed to the intermediate port-wine colour due to neutrality of the mixture. When adding the carbonate, effervescence will be caused by the escape of carbon dioxide gas ; the solution should in this case be kept at a boiling temperature, so as to expel the gas, as otherwise it (the carbon dioxide) obscures the colour reaction with litmus. An inspection of the equations shows that the quantity of the resultant sulphate is the same in both cases.

106. Express in words the meaning of the following equation : $OKH + HCl = KCl + OH_2$.   *S. and A.,* 1878.

107. Explain the following terms : ' analysis,' 'synthesis,' ' mixture,' ' compound,' ' acid,' ' neutral,' ' alkaline.'
    S. and A., 1892.

108. Explain what is implied by the following terminations : *-ous, -ic, -ite, -ate,* and *-ide,* and give examples of their use.   *S. and A.,* 1887.

109. What do you understand by atomicity, and how is it measured ?

110. State why carbon is termed a tetrad element and oxygen a diad element.   *S. and A.,* 1880.

111. Give the atomicity of each element in the following compounds : $HCl - (OH)_2 - NH_3 - CO_2 - SO_2$ and SH_2.
    S. and A., 1877.

$$(OH)_2 = H_2O_2.$$
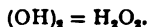
112. Indicate by graphic notation the atomicity of the following elements : nitrogen, sulphur, carbon, chlorine, oxygen, boron, silicon, bromine, phosphorus, zinc, and calcium.
    S. and A., 1879.

113. Why must NO be written as the formula of nitric oxide? and in what way is it an exception to the general rule which governs the active atomicity of elements in a compound? State that rule.

114. Define the terms 'monobasic' and 'dibasic' as applied to acids. Knowing the atomicity of the various metals, write the formulæ of the following salts : silver nitrate, gold chloride, copper nitrate, zinc sulphate, lead chloride, silver sulphate.

115. Give some account of the different varieties of carbon, and mention the uses to which they are applied.

S. and A., 1891.

116. By what experiments can it be shown that charcoal, graphite, and diamond consist essentially of the same material?

S. and A., 1892.

117. What is coke, and how is it made? Explain the difference noticeable in the burning of coke and the burning of coal. Why does coke leave more ashes than the coal from which it is made? *L. U. M.*, 1892.

The student should bear in mind that coal contains not only carbon, but also hydrogen. On being heated the coal evolves hydrocarbons in the vaporous condition, and therefore burns with luminous flame (see Chapters XIV. and XV.). As 100 grams of coal produce a much less weight of coke, which coke contains the whole of the ash of the original coal, it is evident that the coke must contain the higher percentage of ash.

118. If air contains 21 per cent. by volume of oxygen, how many litres of it at standard temperature and pressure are required to burn completely 18 grams of carbon, and what would be the volume of the product formed? (Weight of $11\cdot2$ litres of O = 16 grams.) *S. and A.*, 1886.

119. Classify the following substances as elements and compounds : chalk, graphite, water, sulphur, iron, ammonia, oil of vitriol, chlorine, diamond, ozone. *S. and A.*, 1887.

120. State which of the following substances are elements and which are compounds, and express their chemical composition by symbols or formulæ : ozone, ammonia, water, lime, diamond, nitric acid, sulphur, graphite, marble, nitre.

S. and A., 1891.

121. Express in words the meaning of the following equation : $Ca(HO)_2 + CO_2 = CO(CaO_2) + OH_2$.

S. and A., 1874.

121A. Quicklime is slaked with water, diffused through more water, and filtered. When carbonic anhydride gas is passed through the filtered liquid, it becomes very turbid : what is the composition of the substance which causes the turbidity? Give an equation. *S. and A.*, 1879.

122. You are required to prove that carbon dioxide (carbonic acid gas) is formed when wood is burnt : describe and sketch the apparatus you would use. *S. and A., Pract.*, 1881.

123. Describe the preparation of carbon dioxide, and give a sketch of its properties.

124. A piece of marble is placed in dilute hydrochloric acid. Explain why it disappears, and state the change which the marble and the acid undergo.   ·*S. and A.*, 1889.

125. Express the following changes by equations :—
   (*a*) The action of hydrogen chloride solution on chalk.
   (*b*) The action of diluted sulphuric acid on iron.
   (*c*) The action between caustic soda and sulphuric acid.
   (*d*) The action of chlorine on water at a high temperature.
                                      L. U. M., 1890.

126. Describe experiments with carbon dioxide to show (*a*) its density ; (*b*) its solubility in water; (*c*) its action on lime-water.   *S. and A.*, 1892.

127. Why is carbon dioxide frequently called carbonic acid ? Describe (with sketch) the apparatus you would make use of to prepare this gas in a dry state.   *L. U. M.*, 1892.

128. Describe experiments by which you are led to believe that coal-gas contains hydrogen, that common salt contains chlorine, and that white marble contains carbon.
                                      L. U. M., 1892.

129. Calculate the weight of pure marble that must be treated with hydrochloric acid in order to afford 100 c.c. of carbon dioxide measured at 0° C. and 760 mm. (Ca = 40 ; C = 12.)   *L. U. M.*, 1887.

130. Ten grams of hydrochloric acid (HCl) act on zinc, and the same weight acts on calcium carbonate : what bulk of gas, measured at the normal temperature and pressure, is produced in each case?   *S. and A.*, 1886.

131. You boil common well-water for a few minutes, and observe the separation of a white precipitate : how do you explain the formation of the precipitate? How would you test your explanation by experiment?

132. What do you understand by the terms 'hard' and 'soft' as applied to water? Explain the difference between permanent and temporary hardness.   *L. U. M.*, 1889.

133. The hard water of our chalk districts is rendered soft by the addition of lime-water : explain fully why lime-water is able to produce this result.

134. How are the two oxides of carbon prepared, and by what tests may they be recognised ? *S. and A.*, 1887.

135. How is carbon monoxide prepared? Describe and explain the tests by which you would recognise it. *L. U. M.*, 1888.

136. State any facts known commonly which suggest that the air is concerned in the changes which attend the combustion of coal in an ordinary fire. Describe any experiments you have witnessed which afford proof that such is the case.
L. U. M., 1891.

137. Explain the blue flame seen upon a blacksmith's fire. What effects, if any, would be produced by blowing steam, together with air, into the fire? *L. U. M.*, 1890.

Carbon monoxide is formed from the oxygen of the air when blown through a red-hot mass of coke. Steam under similar circumstances is decomposed with the production of carbon monoxide and free hydrogen.

$$H_2O \ + \ C \ = \ CO \ + \ H_2.$$
Water. Carbon.   Carbon   Hydrogen.
             monoxide.
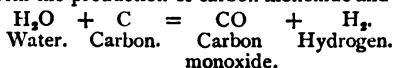
138. How do coal and coke differ from each other in composition ? What are the products obtained when (*a*) air and (*b*) steam are separately passed over red-hot coke? *L. U. M.*, 1888.

139. Represent by equation. and otherwise describe, what happens when oxalic acid is heated with strong sulphuric acid. *S. and A.*, 1879.

140. Oxalic acid is heated with sulphuric acid : how would you experimentally prove that the gases evolved are carbonic anhydride (CO_2) and carbonic oxide (CO)?
S. and A., Pract., 1880.

141. Describe the properties of carbon monoxide (carbonic oxide). Under what conditions is it formed as a product of combustion, and why is it important to ensure the removal of the products of combustion by a proper ventilating pipe when gas is burnt for heating purposes ? *L. U. M.*, 1891.

142. Lime-water is shaken up in a jar filled with carbonic oxide : what occurs? The carbonic oxide is then inflamed, and the lime-water once more shaken up with the contents of the jar : what now takes place ? *S. and A.*, 1875.

143. Describe two experiments to show the properties of (1) carbon monoxide, and (2) carbon dioxide. How would you convert the carbon dioxide into the monoxide, and what relation

would the volume of the monoxide formed bear to that of the dioxide from which it was made?   *S. and A.*, 1890.

144. 100 c.c. of air are passed over red-hot charcoal : how would you ascertain if the air was altered in volume or had experienced any alteration in properties?   *S. and A.*, 1887.

The exact measurement in an experiment of this kind is somewhat difficult, as both before and after the passage over charcoal the tempera- ture and pressure of the gas require to be observed and allowed for. The best form of apparatus would consist of a tall cylinder graduated in c.c. for holding the air at the commencement of the experiment. This should be fitted with a cork carrying a thistle funnel leading to the bottom of the vessel, and a delivery tube. The leading tube is attached to a tube containing charcoal heated red hot in a tube-furnace. The outlet end of this tube is conveyed into a pneumatic trough con- taining mercury, in which is inserted another graduated cylinder arranged for the collection of the gas. Mercury is now poured through the thistle funnel of the first flask until the air just commences to escape into the reception cylinder. The height of the mercury in each cylinder is then measured, and mercury is slowly poured into the first one until 100 c.c. of air have been forced through the tube. The volume in the second cylinder should now be read, less the amount of air it contained at the commencement of the experiment. The differ- ence in temperature may be neglected unless extreme accuracy is re- quired, as both quantities of air speedily acquire the temperature of the room ; otherwise a thermometer must be introduced into each vessel and a correction made for temperature. In order to make a correction for the pressure to which each lot of air is subject, measure first the height in millimetres which the column of mercury stands in the tube of the thistle funnel above the level of the liquid in the jar itself. Suppose this height to be 50 mm., and assuming the barometer to be standing at 760 mm., then the air in the flask is under a pressure of 760 + 50 = 810 mm. ; from this its volume at normal pressure is easily calculated. The readiest plan with the air in the reception jar is to depress the jar in the mercury until the level of the mercury in the jar is the same as that in the trough ; the air is then under barometric pressure. The volume is then read, and that before the action of char- coal may be compared with that after.

As one molecule of oxygen produces two molecules of carbon monoxide, and there are about 21 c.c. of oxygen in 100 c.c. of air, there will be an increase in volume of about 21 c.c. as the result of the passage over red-hot charcoal.

145. How may it be shown that the gases named carbon monoxide and carbon dioxide contain different proportions per cent. by weight of carbon?   *L. U. M.*, 1891.

The proportion by weight of carbon in the dioxide is determined by passing oxygen over a weighed quantity of red-hot carbon, and weighing the resultant carbon dioxide. The carbon is introduced into a tube heated in a furnace, having its exit end packed with fragments

of copper oxide, CuO ; on passing oxygen, combustion ensues, and any monoxide produced is converted into the dioxide during its passage over the copper oxide. The escaping gas is led into a weighed tube containing fragments of caustic potash, KHO, by which it is absorbed. The difference in weight of this tube before and after the experiment gives the weight of carbon dioxide produced.

On exploding carbon monoxide with excess of oxygen in a eudio-meter, and subsequently absorbing the resultant dioxide by caustic potash, the composition of the gas may be ascertained. It will be found that two volumes of the monoxide combine with one of oxygen and produce two volumes of the dioxide. From these data the weight may be indirectly determined. A direct determination of weight may be made by passing a known volume of the monoxide (knowing its density) over red-hot carbon monoxide, absorbing the dioxide produced with caustic potash, and then weighing.

146. By what experiments can you show that in carbonic oxide the proportion of carbon to oxygen is twice as great as in carbon dioxide? *S. and A.*, 1892.

147. Ten grams of oxalic acid are heated with sulphuric acid : what weight of carbon monoxide is evolved? If the resultant mixed gases be passed through a tube containing red-hot charcoal, so as to effect the complete conversion of the carbon dioxide into carbon monoxide, what weight of carbon monoxide will be produced ?

148. How many volumes of carbon dioxide (carbonic acid gas) will be formed when a mixture of four volumes of carbon monoxide (carbon oxide gas) and four volumes of oxygen is burnt? State what volume of oxygen, if any, remains uncom-bined. *S. and A.*, 1881.

149. One volume of carbon monoxide (carbonic oxide) gas is mixed with two volumes of oxygen, and an electric spark passed through the mixture : what volume of carbon dioxide gas (carbonic anhydride) is formed, and what volume of oxygen left? *S. and A.*, 1877.

150. How is marsh-gas prepared, and what are its general properties?

151. How is olefiant gas prepared? Mention the distin-guishing characteristics of this compound. By what means could you convince yourself that this gas contains twice as much carbon as an equal bulk of marsh-gas does ?

152. Describe the preparation and properties of olefiant gas. How is it proved that its molecule contains two atoms of carbon? *L. U. M.*, 1887.

153. How is olefiant gas made? What volume of it would be equal in weight to 10 litres of marsh-gas? *L. U. M.*, 1889.

154. How may it be proved that any given volume of ethylene (olefiant gas) contains twice as much carbon as an equal volume of marsh-gas, but the same amount of hydrogen?
L. U. M., 1892.

155. Explain exactly what is implied by the formula C_2H_4.
L. U. M., 1885.

156. How much pure air ought to be mixed with 100 measures of fire-damp (marsh-gas) in a coal-mine in order to supply material for the complete combustion of marsh-gas during explosion?

The combustion of marsh-gas is represented by the following equation:—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

One volume of marsh-gas requires two volumes of oxygen; therefore 100 measures will require 200 measures of pure oxygen.
Air contains 21 per cent. by volume of oxygen; therefore—

As 21 : 200 : : 100 : 952 volumes of pure air.

157. How much oxygen do you require for the complete combustion of 10 c.c. of marsh-gas? How many cubic centimetres of each product of combustion would be formed?

158. A gaseous mixture consisting of 100 volumes of carbon monoxide and 150 volumes of oxygen is confined over mercury; an electric spark is passed through the mixture, and a ball of caustic potash is then brought into the gas: describe the chemical changes which occur, and state what volume (if any) of gas remains at the end of the operation. (Caustic potash possesses the property of absorbing carbon dioxide gas.)

159. To burn 16 grams of acetylene, how many cubic centimetres of oxygen will be required, and what will be the volume of the products of combustion?

160. State what volume of oxygen will be required for the combustion of 250 c.c. of each of the following gases; state also the volume of the products of combustion in each case: hydrogen, carbon monoxide, marsh-gas, acetylene, ethylene, ammonia, and sulphuretted hydrogen.

161. How many volumes of air are required for the complete combustion (*a*) of one volume of marsh-gas, and (*b*) of one volume of olefiant gas? Specify the composition by volume of the products in each case.   *L. U. M.*, 1886.

162. Ten measures of ethylene are mixed with 50 measures of oxygen, and the mixture is fired by an electric spark : what volume of gas remains after the explosion ? of what does this gas consist ? and how would you demonstrate the proportions of the constituents present in this residual gas ? *L. U. M.*, 1890.

163. On heating water for a bath in a large copper vessel by means of one of the so-called air-gas burners now frequently used, it is noticed that liquid appears on the outer surface of the vessel above the flame : what simple experiments could you make in order to show that this liquid consists of nearly pure water ? How is the appearance of water in such a case to be accounted for ? *L. U. M.*, 1890.

164. Both water and carbon dioxide are formed when coal-gas burns : describe, and show by sketch, how you would prove this to be the case. *S. and A.*, 1886.

165. Define ' combustion,' and state clearly what you understand by that term.

166. Define the terms ' combustible ' and ' supporter of combustion : ' describe an experiment to show that they are purely relative.

167. How may oxygen be caused to burn in either hydrogen or coal-gas ? Explain the terms ' complete combustion ' and ' incomplete combustion.' *L. U. M.*, 1892.

Incomplete combustion may occur when there is a deficiency of oxygen ; thus when carbon is burned to the monoxide, there is an example of incomplete combustion.

168. Give some account of the nature and composition of ordinary fuel. State fully the chemical changes which occur in the combustion of coal. *L. U. M.*, 1887.

169. If 100 parts by weight of air contain 23 of oxygen and 77 of nitrogen, how many tons of air would be needed to burn one ton of coal, consisting of ?—

Carbon	.	.	.	90·55
Hydrogen	.	.	.	4·14
Nitrogen	.	.	.	1·26
Oxygen	.	.	.	2·35
Ash	.	.	.	1·70
				100·00

Assume that, on burning, the carbon is wholly converted into

carbon dioxide, and the hydrogen into water ; that the nitrogen is evolved as such, and that the ash is already fully oxidised.

L. U. M., 1885.

The quantity of oxygen present in the coal must be deducted from the amount found necessary to burn the carbon and the hydrogen.

170. A certain metallurgical operation absorbs one million units of heat : how many grams of each of the following substances respectively would require to be burned in oxygen to furnish the necessary quantity of heat : hydrogen, carbon, carbon monoxide, olefiant gas, and alcohol ?

171. Why does olefiant gas burn with a brighter flame than hydrogen ?

172. Describe the structure of the flame of a common candle, and explain why carbon is set free by the combustion in the interior, but not on the surface of the flame.

173. Give some account of the structure of flame, and explain the principle of the Davy lamp.   *L. U. M.*, 1889.

The Davy lamp is used by the miner as a source of light where there is danger of the atmosphere containing an inflammable mixture of gases. It consists essentially of an ordinary oil-lamp completely enveloped in a casing of fine wire gauze ; such gauze prevents the passage of flame through it.   This may be readily tested by depressing a piece of fine gauze over a Bunsen flame ; the flame does not pass through the gauze, but the gas above it burns on a light being applied. If the gas below be extinguished, and then again turned on, the gas may be kindled *above* the gauze, and the flame will not descend through. It will be readily understood that the gauze envelope of the Davy lamp operates in a similar manner. The effect is due to the rapid cooling effect produced by the conductive power of the gauze ; by this means the temperature of the burning gases is reduced below that necessary for combustion.

174. Explain fully why the flame of a common gas-light is brighter than the flame from a Bunsen burner. What special advantages does the latter possess ?

175. If you place the chimney glass over the flame of a reading-lamp the flame increases in brightness : why does it do so ? If you blow a current of air into the flame of an ordinary candle, the flame appears less bright than it did before the introduction of the air : explain why this is the case.

176. Describe two processes for the preparation of nitrogen, one suitable for the production of small and the other of large quantities of the gas.   *L. U. M.*, 1889.

177. Write an account of the principal properties of nitrogen.

What effect is produced by passing a series of electric sparks through a mixture of nitrogen and oxygen ?

178. How would you distinguish the following gases from one another : chlorine, oxygen, nitrogen, carbon monoxide, marsh-gas, olefiant gas? *L. U. M.*, 1888.

179. What is the composition of the atmosphere, and how may it be determined (1) by volume, (2) by weight?

180. By what experiments can you prove that the air contains four-fifths of its volume of nitrogen ? *S. and A.*, 1887.

181. Name the principal gases in the air. How is their amount determined ? *S. and A.*, 1888.

182. Explain as fully as you can why air is said to be a mixture of two elements, and hydrochloric acid a chemical combination of two elements. *S. and A.*, 1890.

183. How can you prove that the constituents of the atmosphere are merely mechanically mixed and not chemically combined ? *L. U. M.*, 1887.

184. Why is the flame of a taper extinguished in nitrogen gas, and why does it continue to burn in air ? *S. and A.*, 1887.

185. Describe three experiments, the best you can think of : one is to prove that the air contains oxygen, another that it contains carbon dioxide, and the third that it contains aqueous vapour. *S. and A.*, 1881.

186. In what respects does the air in a crowded room differ from fresh air ? *S. and A.*, 1889.

187. Describe an experiment illustrating the action of plants in sunlight on carbon dioxide. *L. U. M.*, 1886.

188. What volume of water vapour results from the explosion of a mixture of two volumes of hydrogen and one volume of oxygen ? Explain how the fact that one volume of oxygen unites with two volumes of hydrogen to form water may be made use of in order to determine the amount of oxygen in the air.
L. U. M., 1887.

189. Fifty measures of air were mixed with 30 measures of hydrogen gas, and fired by an electric spark ; after cooling, 48·8 measures of gas remained : what volume of oxygen was present in the air examined ? *L. U. M.*, 1888.

190. Calculate the weight of 10 litres of air (measured at 0° C. and 760 mm.) containing 21 per cent. of oxygen and 79 per cent. of nitrogen. *L. U. M.*, 1888.

191. Describe the mode of preparation of ammonia gas. What are its principal properties, and how may its composition be determined?   *S. and A.*, 1892.

192. How is ammonia prepared? Describe the means by which you would demonstrate the volumetric composition of the gas.   *L. U. M.*, 1889.

193. What takes place when a lighted taper is immersed in gaseous ammonia?   *S. and A.*, 1874.

194. Ammonia gas is led into solution of hydrochloric acid : what is produced? Give an equation. The resulting liquid is evaporated to dryness in a porcelain crucible, which is afterwards heated to redness : what will remain in the crucible?

S. and A., 1879.

195. Write equations showing the action of hydrochloric acid on (*a*) caustic soda (sodium hydrate) ; (*b*) sodium carbonate ; and (*c*) ammonia gas. Name the several products.

L. U. M., 1888.

196. What volume of oxygen is required for the complete combustion of one volume of each of the following gases : hydrogen, carbon monoxide, ammonia, and marsh-gas? *L. U. M.*, 1887.

197. How can you demonstrate that ammonia is composed of nitrogen and hydrogen?   *S. and A.*, 1886.

198. What is the percentage composition of ammonic chloride?   *S. and A.*, 1876.

199. By what experiments could you show that hydrogen was a constituent of hydrochloric acid, sulphuric acid, and ammonia?   *S. and A.*, 1889.

200. Express in words what is implied in the following equations :—

$$(a) \qquad Zn + H_2SO_4 = ZnSO_4 + H_2.$$
$$(b) \qquad CaCO_3 = CaO + CO_2.$$
$$(c) \qquad 2NH_4Cl + CaO = 2NH_3 + H_2O + CaCl_2.$$
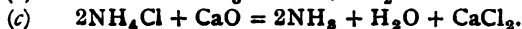
S. and A., 1888.

201. Complete the following equations :—
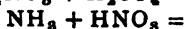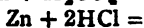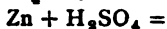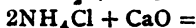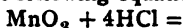
$$MnO_2 + 4HCl =$$
$$2NH_4Cl + CaO =$$
$$Zn + H_2SO_4 =$$
$$Zn + 2HCl =$$
$$NH_4NO_3 + H_2SO_4 =$$
$$NH_3 + HNO_3 = \qquad \textit{S. and A.}, 1891.$$

202. Give an account of the various methods by which a gas might be liquefied, illustrating your description by the examples of ammonia, oxygen, and carbon dioxide.

L. U. M., 1886.

Cailletet liquefied oxygen by first highly compressing the gas, cooling it to as low a temperature as possible, and then allowing it to suddenly expand. The sudden absorption of heat reduced the temperature so low that the gaseous oxygen condensed to a liquid.

203. Define a compound radical, and give an example.

S. and A., 1875.

204. How is nitric acid usually prepared? What are its properties, and by what reactions can it be distinguished from hydrochloric acid and sulphuric acid? *S. and A.,* 1890.

205. Prove by chemical equations that more nitric acid can be obtained from sodium nitrate than from an equal weight of potassium nitrate. *S. and A.,* 1891.

206. Explain in words all that is expressed by the following equation:—

$$2KNO_3 + H_2SO_4 = 2K_2SO_4 + 2HNO_3.$$
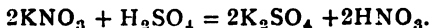
S. and A., 1881.

207. How many pounds of nitric acid can be obtained from 150 pounds of nitre (potassium nitrate), and how many grains of sulphuric acid will be needed? *S. and A.,* 1879.

208. I put some gold-leaf into a jar of nitric acid and into one of liquid hydrochloric acid: what takes place? I mix the contents of the two jars: what then occurs?

S. and A., 1876.

209. How would you distinguish hydrochloric acid from nitric acid? Give the formulæ of the two acids, and describe the preparation of a salt of each acid. *S. and A.,* 1887.

210. What weight of pure nitric acid would contain 100 grams of oxygen; and what weight of pure hydrochloric acid would contain 100 litres of chlorine at the standard temperature and pressure? *S. and A.,* 1889.

211. A solution of nitric acid of specific gravity 1·46 contains 80 per cent. of HNO_3: what weight of this solution is theoretically required to dissolve 10 grams of copper oxide?

212. What changes take place when zinc dissolves in dilute nitric acid? *S. and A.,* 1876.

213. Carbonate of ammonia and nitric acid are given to

you : how would you prepare nitrous oxide from these ?   Draw a sketch of the apparatus you would use, and give an equation showing the decomposition which takes place in making the gas.   *S. and A.*, 1879.

214. How is pure nitrous oxide made ?   By what characters or tests can it be distinguished from oxygen and from nitric oxide respectively ?   *S. and A.*, 1891.

215. How is the compound N_2O prepared ?   Explain the process and state the means you would adopt to determine its composition and molecular weight.   *L. U. M.*, 1885.

216. Describe the preparation of nitrous oxide gas.   A mixture of equal volumes of nitrogen and oxygen has nearly the same effect upon flame as nitrous oxide : how would you distinguish by experiment the mixture from the compound ?
L. U. M., 1891.

217. A lighted taper burns brilliantly when plunged into a jar of gas.   What gases are capable of producing such effect, and how would you determine what gas was present in any particular case ?   *S. and A.*, 1890.

218. Why are the nitrogen and oxygen in nitrous oxide said to be in a state of combination, and why in air are they said to be in a state of mixture ?   *S. and A.*, 1888.

219. How could you obtain nitrogen from (1) ammonia, (2) nitrous oxide, and (3) air ?   *S. and A.*, 1889.

220. What are the principal properties of nitrogen monoxide?   Feebly burning sulphur is extinguished when plunged into this gas, while, if brightly burning, it continues to do so with increased brilliancy : state clearly the reason for this.

221. Ten grams of nitric acid are neutralised by ammonia : what weight of nitrogen monoxide may be obtained from the ammonium nitrate thus produced ?

222. Calculate the weight of ammonium nitrate which must be decomposed in order to afford one litre of nitrous oxide gas, measured at 15° C. and under 740 mm. pressure.
L. U. M., 1886.

223. How would you prepare nitrous and nitric oxides ? Give equations for the reactions, and state how you would recognise these bodies.   *S. and A.*, 1886.

224. How are the two lowest oxides of nitrogen (nitrous and nitric oxides) prepared ?   By what properties are they

distinguished? How could you prove the volumetric composition of the two oxides? *L. U. M.*, 1886.

225. State what is observable when saltpetre is distilled with sulphuric acid, and also when a portion of the product is poured on to some copper in a test-tube. *L. U. M.*, 1892.

226. Describe the effect, if any, noticeable when nitric oxide gas is mixed with dry oxygen, with oxygen confined over water, and with nitrous oxide respectively. Afterwards explain the changes by equations. *L. U. M.*, 1892.

227. By what properties would you recognise nitric oxide? Compare its power of supporting combustion with that of nitrogen monoxide.

228. Two bottles are placed before you, each containing a colourless gas. On removing the stoppers, colourless steamy fumes escape from the one (*a*), and orange-red vapour from the other (*b*). What might each of these gases be, and how would you further test it in order to identify it with certainty?

L. U. M., 1890.

229. I want 6 grams of nitric oxide : how much copper and nitric acid shall I require for its production ?

230. Nitric acid is poured upon copper, hydrochloric acid upon chalk, and sulphuric acid into water. What are the chemical changes which occur in each case, and the appearances which accompany each reaction? *S. and A.*, 1890.

231. Express in the form of equations the action of—
       (1) Heat upon mercuric oxide.
       (2) Sulphuric acid upon common salt.
       (3) Hydrochloric acid upon marble.
       (4) Nitric acid upon copper.
       (5) Steam upon red-hot iron. *S. and A.*, 1887.

232. Give an account of the mode of preparation and properties of nitrous acid. *L. U. M.*, 1887.

233. What sulphur compounds occur in nature? Describe the chief properties of sulphur, and state how it may be converted into its various allotropic modifications. *S. and A.*, 1888.

234. How is sulphur commonly obtained? Give an account of the action of heat on sulphur. *L. U. M.*, 1888.

235. By what tests could you prove that a substance which was stated to be sulphur actually was that element?

S. and A., 1889.

236. What is meant by the term 'allotropy'? Describe the various allotropic modifications of sulphur, oxygen, and carbon.
S. and A., 1887.

237. Explain what is meant by 'chemical combination in definite and in multiple proportions.' Give illustrations from carbon or sulphur compounds.   *S. and A.*, 1886.

238. Describe an experiment by which you can show that when a piece of charcoal or sulphur is burnt in the air the substance of the charcoal or sulphur is not destroyed, but only changes its form.   *S. and A.*, 1891.

239. With what bodies will sulphur, chlorine, and carbon dioxide combine? Give the formulæ for the compounds formed.   *S. and A.*, 1888.

240. Some purchased milk of sulphur is suspected to be adulterated with plaster of Paris (calcium sulphate). How could you test it, and by a simple process ascertain the amount of the impurity?   *L. U. M.*, 1890.

241. What is the action of heat upon the following substances?—

   (1) Ammonium nitrate.
   (2) Ozone.
   (3) Sulphur.
   (4) Charcoal in presence of (*a*) oxygen; (*b*) carbon dioxide.
   S. and A., 1890.

242. Sketch and describe apparatus used in demonstrating the following facts: (*a*) water is produced by the union of pure oxygen and hydrogen; (*b*) sulphur burned in oxygen does not alter the volume of the gas.   *L. U. M.*, 1890.

243. What volume of atmospheric air (measured at 15° C. and 750 mm.) is required for the complete combustion of one gram of sulphur? (S = 32.)   *L. U. M.*, 1889.

244. What weight of sulphur would you expect to obtain from 10 tons of sulphur ore (ferric sulphide)? Allow what you consider a fair percentage for loss.

245. Describe exactly the preparation of sulphuretted hydrogen, and point out the chief properties of the gas.
L. U. M., 1889.

246. Describe how sulphuretted hydrogen is prepared. By what experiments would you show its properties and demonstrate its composition?   *S. and A.*, 1886.

247. How is sulphuretted hydrogen prepared? What are its properties, and what is formed when it burns in air?
S. and A., 1888.

248. How is sulphuretted hydrogen made? Describe its chief properties, and state how you could prove that it contained its own volume of hydrogen? *S. and A.*, 1889.

249. How is sulphuretted hydrogen prepared? Write equations expressing the changes which take place when the gas is (*a*) mixed with chlorine; (*b*) heated with tin; and (*c*) led through an aqueous solution of sulphurous acid. *L. U. M.*, 1887.

For (*c*) refer to the chapter on sulphur dioxide and sulphurous acid.

250. Sulphuretted hydrogen is passed into solutions of the following substances in different test-tubes: arsenious anhydride, lead acetate, zinc sulphate, antimony chloride, and ferrous sulphate: what is the result in each instance?

251. How could you prove that sulphur was a constituent of sulphuretted hydrogen? What weight of sulphur is contained in 100 grams of sulphuretted hydrogen? *S. and A.*, 1890.

252. Required one litre of sulphuretted hydrogen gas at o° C. and 760 mm. pressure; calculate the weight of iron sulphide necessary for its production. Trace the chemical changes which take place when the gas is led into (*a*) aqueous solution of chlorine, and (*b*) solution of ammonia. *L. U. M.*, 1885.

253. Calculate the weight of 100 litres of hydrogen sulphide, measured at 27° C. and 740 mm. (S = 32.) *L. U. M.*, 1892.

254. Express in the form of equations the action of—

  (1) Heat upon ammonium nitrate.
  (2) Hydrogen upon (*a*) cold, (*b*) hot copper oxide.
  (3) Sulphuric acid upon ferrous sulphide.
  (4) Hydrochloric acid upon chalk.
  (5) Sulphuric acid upon nitre. *S. and A.*, 1888.

255. Classify the following substances as solids, liquids, and gases: ozone, nitric acid, graphite, nitric oxide, ammonia, nitre, sal ammoniac, hydrogen chloride, sodium chloride, nitrous oxide, calcium carbonate, ferrous sulphide. *S. and A.*, 1892.

256. Describe and explain, with equations, the methods of preparing sulphur dioxide from (*a*) sulphur, (*b*) sulphuric acid, (*c*) a sulphite. *L. U. M.*, 1889.

257. How is sulphur dioxide made? How can you prove that it contains its own volume of oxygen? *S. and A.*, 1886.

258. Describe the modes of origin and properties of sulphur dioxide. How could you demonstrate the volumetric composition of the gas ? *L. U. M.,* 1886.

259. What bodies are formed when sulphur burns in (*a*) air, (*b*) hydrogen ? Express the changes which occur by means of chemical equations, and describe the characteristic properties of the products. *L. U. M.,* 1886.

260. What are the principal uses of sulphur dioxide ?

261. Name any bodies formed by the action of sulphuric acid, concentrated and dilute, hot and cold, upon the following substances : sodium chloride, zinc, copper, nitre, and oxalic acid. Give equations in each case. *L. U. M.,* 1886.

262. Arrange the following gases in the order of their solubility in water : oxygen, carbon dioxide, hydrogen, nitric oxide, nitrous oxide, sulphur dioxide, chlorine, sulphuretted hydrogen, ammonia. *S. and A.,* 1891.

263. What is a chemical equation ? Give in the form of chemical equations the action of—

(1) Sulphuric acid upon common salt.
(2) Sulphuric acid upon copper when heated.
(3) Sulphuric acid upon an aqueous solution of ammonia.
S. and A., 1889.

264. Complete the following equations :—
$$Cu_3 + 8HNO_3 =$$
$$2NH_4Cl + CaH_2O_2 =$$
$$Cu + 2H_2SO_4 =$$
$$C + 2H_2SO_4 = \qquad S.\ and\ A.,\ 1890.$$

265. Complete the following equations :—
$$FeS + H_2SO_4 =$$
$$Cu + 2H_2SO_4 =$$
$$Zn + H_2SO_4 =$$
$$Na_2CO_3 + H_2SO_4 =$$
$$Na_2SO_3 + H_2SO_4 =$$
$$NaCl + H_2SO_4 = \qquad S.\ and\ A.,\ 1892.$$
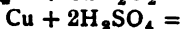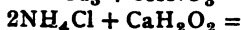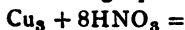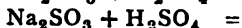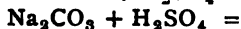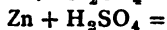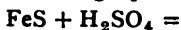
266. How would you prepare sulphur trioxide, and what are its properties ? Give a sketch of the apparatus.

267. How could you convert sulphur dioxide into sulphuric acid, and sulphuric acid into sulphur dioxide ?
S. and A., 1887.

268. How can sulphurous acid be converted into sulphuric

acid, and how can sulphuric acid be converted into sulphurous acid? How could you distinguish a sulphite from a sulphate?
S. and A., 1889.

269. What are the principal properties and uses of sulphuric acid?

270. I lb. of sulphur may combine with I lb. of oxygen or with 1½ lb. of oxygen: what compound is formed in each case? If no other compounds of sulphur and oxygen are known, how does the existence of these two only illustrate the law of multiple proportions? *S. and. A.*, 1891.

271. What are the properties common to acids? In what respects does sulphurous acid differ from sulphuric acid?
S. and A., 1892.

272. What volume of sulphur dioxide is formed by burning 10,000 litres of hydrogen sulphide, and how many kilograms of sulphuric acid, H_2SO_4, are theoretically producible therefrom? ($S = 32$; $O = 16$.) *L. U. M.*, 1891.

273. Calculate the weight of sulphur required to afford 100 tons of sulphuric acid. Briefly explain the method by which sulphuric acid is made. ($S = 32$.) *L. U. M.*, 1888.

274. How much zinc must be dissolved in dilute sulphuric acid in order to produce 40 lbs. of crystallised zinc sulphate ($ZnSO_4, 7H_2O$)? *S. and A.*, 1892.

275. Name the substances having the following formulæ:
H_2S, NH_3, CO, H_2CO_3, NO, NO_2, SO_3, O_3. *S. and A.*, 1889.

276. Give the formulæ for three carbonates, three sulphates, three sulphites, and three nitrates. *S. and A.*, 1886.

277. How is bromine prepared? In what forms does it commonly occur in nature? Give some account of the chief properties of bromine and of the tests by which it may be recognised. *L. U. M.*, 1887.

278. Two bottles are given you; one contains vapour of bromine, and the other vapour of nitric peroxide (NO_2): how would you ascertain which of the two contains bromine?

279. Complete the following equations:—

$$(a) \qquad HNO_3 + NH_3 =$$
$$(b) \qquad 2HCl + Na_2CO_3 =$$
$$(c) \qquad 2NaBr + Cl_2 =$$
$$(d) \ NaNO_3 + NaHSO_4 =$$
$$(e) \qquad Na_2SO_3 + H_2SO_4 = \textit{L. U. M.,} \ 1891.$$
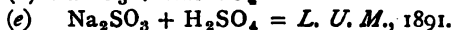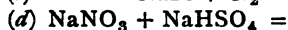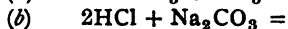
280. Explain what occurs when a current of chlorine is passed through a solution of potassium iodide. How would you prove a brown liquid to be an aqueous solution of iodine?

281. Two aqueous solutions are given you; one contains free bromine only, the other free iodine only : describe how you would prove the presence of the bromine in the one solution, and of the iodine in the other.

282. Two solids are given to you, one of which may be graphite, the other iodine : describe in detail the physical and chemical experiments you would make in order to identify these two substances. *L. U. M.*, 1890.

283. Describe exactly how you would use a solution of iodine for the detection of starch. If the solution of iodine be first rendered alkaline by the addition of caustic potash, will it still answer the purpose? if not, why not?

284. Describe the action of heat upon (*a*) iodine, (*b*) nitric acid, (*c*) ammonia solution. *L. U. M.*, 1890.

285. Specify the common sources of the elements chlorine, bromine, and iodine ; explain, with the aid of equations, the methods adopted for their liberation, and state how you would distinguish between aqueous solutions of each of the free elements. *L. U. M.*, 1885.

286. Chlorine, bromine, and iodine are said to be members of one family of elements ; make a comparison of their properties and of their chief compounds so as to show why they are so described. *L. U. M.*, 1892.

287. How is hydrofluoric acid prepared, and what is its action on glass?

288. What volume of chlorine at normal temperature and pressure would be required ?—

   (*a*) To combine with 10 litres of olefiant gas.
   (*b*) To decompose 10 litres of sulphuretted hydrogen, liberating the sulphur ;
   (*c*) To decompose 10 grams of potassium iodide. (K = 39.) *L. U. M.*, 1889.

289. If hydrogen sulphide is passed into a mixture of iodine and water, sulphur is deposited and hydrogen iodide formed ; the iodine may be in turn displaced from combination by bromine, and the bromine by chlorine : what weight of each of these elements would be required to displace the sulphur

contained in 100 grams of hydrogen sulphide? (S = 32 ; I = 127 ; Br = 80 ; Cl = 35·5.) *L. U. M.*, 1891.

290. By what tests or chemical reactions could you distinguish carbonate of lime from fluor-spar? *L. U. M.*, 1886.

291. What is the action of sulphuric acid on the following substances : limestone, copper, zinc, fluor-spar, and common salt? Represent the reactions by equations, and very briefly describe the chief properties of the products. *L. U. M.*, 1885.

292. Trace the phosphorus of commerce back to its original and ultimate source.

293. How is phosphorus prepared? Describe the two chief varieties of phosphorus, and state how they may be converted one into the other. *L. U. M.*, 1889.

294. Describe the characteristic properties of common and of red phosphorus ; and state the conditions under which the white is turned into the red, and the red into the white variety.
L. U. M., 1891.

295. By what experiments would you distinguish ordinary phosphorus from amorphous phosphorus, graphite from iodine, chlorine from ozone, carbon dioxide from nitrogen?
S. and A., 1888.

296. Explain the chemical action which takes place when phosphorus and caustic potash solution are boiled together. What are the properties of the gas evolved? How do you account for ordinary phosphoretted hydrogen losing its property of spontaneous inflammability when kept for some time at a low temperature ?

297. How is phosphoretted hydrogen prepared? Describe its chief properties. What is formed when it burns in the air? In what respects does it resemble ammonia?
L. U. M., 1887.

Phosphoretted hydrogen resembles ammonia in the constitution of its formula ; it forms one or two compounds analogous in composition to those produced by the combination of ammonia with acids. Of these, phosphonium iodide is an example. Its similarity to the corresponding ammonia compound is shown in the following equations :—

$$NH_3 \quad + \quad HI \quad = \quad NH_4I.$$
Ammonia.   Hydriodic acid.   Ammonium iodide.

$$PH_3 \quad + \quad HI \quad = \quad PH_4I.$$
Phosphoretted   Hydriodic   Phosphonium
hydrogen.   acid.   iodide.
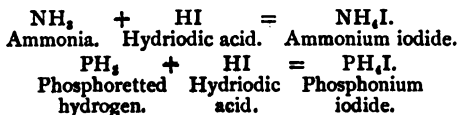
298. How is phosphoretted hydrogen gas prepared? Give an account of its properties, and calculate the volume of air required for the complete combustion of one litre of the gas.

L. U. M., 1886.

299. Which of the following gases burn in air, and in which will the flame of a taper be extinguished : carbon dioxide, nitrous oxide, nitric oxide, carbonic oxide, sulphuretted hydrogen, marsh-gas, hydrogen, oxygen, nitrogen, sulphur dioxide, ammonia, hydrochloric acid, and phosphoretted hydrogen?

L. U. M., 1887.

300. Write the formula of common phosphoric acid. Describe and explain its usual mode of preparation, and the tests by which it can be identified. *L. U. M.*, 1888.

301. Give some examples, with formulæ, of 'acids,' 'bases,' and 'salts,' and point out the distinctive characters of each group of substances. Cite evidence as to the basicity of common phosphoric acid. *L. U. M.*, 1889.

302. Give a short account of the forms of silica met with in nature, and point out the chief characters ·by which crystallised silica and diamond can be distinguished. *L. U. M.*, 1886.

Diamond is combustible, while silica is non-inflammable.

303. Describe how you would render silica soluble in aqueous hydrochloric acid, and how the soluble modification of this substance can be converted into the insoluble form.

304. Flint is said to be a compound of silica ; the aqueous solution of this substance, although it has no sour taste, is said to contain silicic acid : why is it so called?

305. How would you propose to distinguish between fragments of the following substances : (*a*) graphite, (*b*) iodine, (*c*) diamond, (*d*) silica (quartz)? *L. U. M.*, 1889.

306. The oxides formed by burning carbon, sulphur, and phosphorus in oxygen, and the material of which flint and quartz consist, are all regarded as members of one class of compounds : what properties have those substances in common which have led to their being thus regarded? *L. U. M.*, 1891.

307. Describe carefully any two simple chemical experiments (not referred to in the preceding questions) which you have either made yourself or seen performed. State the object of the experiments, their results, and what you learned from them. *L. U. M.*, 1890.

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